Green Pesticides Handbook
Essential Oils for Pest Control

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Pyrethrum Oils

Publication details
https://www.routledgehandbooks.com/doi/10.1201/9781315153131-21
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Published online on: 30 May 2017

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21.1 Introduction

Synthetic pesticides are an invaluable component of agriculture, which enhance agricultural productivity because in their absence, heavy losses caused by pests would be incurred. For instance, in the United Kingdom wheat yields rose from 2.5 t/ha in 1948 to 7.5 t/ha in 1997 (Cooper and Dobson 2007). As a result, an astronomic increase has been recorded in their use, and to date, more than 1000 substances have been registered as pesticides (Tomlin 2003). However, not all the pesticide reach the target (Pimentel 1992), because they find their way into environmental compartments where their residues can be detected at parts per million, parts per billion, or parts per trillion levels, depending on the persistence of the pesticides (Ccanccapa et al. 2016). Because of that, many regulations, such as the Food Quality Protection Act, have been put in place to control their registration (Dayan et al. 2009). In addition, there has been a paradigm shift toward exploring the use of biopesticides as a viable option to alleviating pesticide pollution. Biopesticides are mainly classified as plant extracts, microorganisms, pheromones, and genes.

Plant-based pesticides, which are also known as botanical pesticides, have gained increasing popularity because they are "green pesticides," which reduce the pest population, while at the same time being environmentally compatible (Koul et al. 2008). They were developed into pesticides by noticing their traditional use in crop protection, checking their efficacy, and consequently identifying the active ingredients (Ntalli and Menkissoglu-Spiroudi 2011). However, their major problem is the great difference in the composition and quality of the plant extracts, which can be natural or due to the extraction technique employed (Miresmailli and Isman 2014). For this reason, they have failed to outcompete synthetic pesticides in the field of plant protection. Moreover, it has been suggested that their greatest benefit can be realized in developing countries, where the plants are locally available at a low cost, compared with in industrialized nations, where legislation is very stringent and they cannot be registered easily (Isman 2008).

Examples of these include neem (*Azadirachta indica* A. Juss), pyrethrum (*Chrysanthemum cinerariaefolium*), and nicotine (*Nicotiana tabacum*) (Singh et al. 2010). They can be classified according to their modes of action as antifeedants, attractants, antimicrobials, fumigants, contact toxicants, or repellents (Akhtar and Isman 2012; Miresmailli and Isman 2014). Pyrethrum is an example of an antifeedant that disturbs the feeding process of insects (Akhtar and Isman 2012).

The insecticidal value of pyrethrum flower was discovered by the Chinese more than 2000 years ago (Singh et al. 2010). However, its use was only fully realized after an American trader, Jumticoff, discovered its use in the control of lice by the Caucuses tribes (Schleier and Peterson 2011). Since then, production increased in the Dalmatia Coast, followed by Japan (Anon 2010). However, after World War II, increased production was observed in Kenya. By the 1960s, Kenya supplied more than 90% of the world's pyrethrum. However, the production dropped around 2004, and since that time, the island state of Tasmania in Australia has dominated with 65% of the world production (Monda 2014). In addition, production has steadily increased in countries like Rwanda, China, and Tanzania, as shown by Figure 21.1.

Currently, pyrethrum plants are found in countries such as Kenya (Wandahwa et al. 1996), India (Bhakuni et al. 2007), Tanzania, Ecuador, Brazil, Russia, Japan (Srivastava et al. 2010), and Australia (Morris et al. 2006). The plantations in Tasmania, Australia, have become the second largest producers after Kenya, producing plants almost similar to those found in East Africa (Isman 2006). However, the plants obtained in India produce

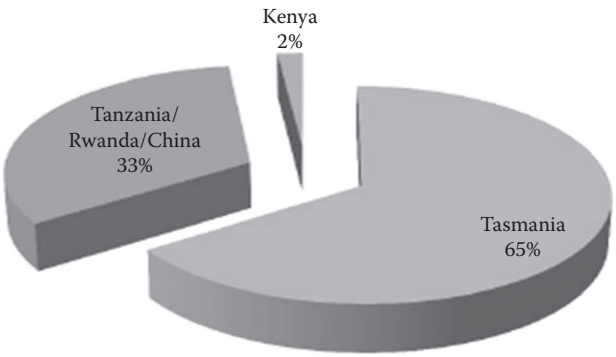

FIGURE 21.1
World production of pyrethrum flowers 2011–2012 (pale refined extract 50%). (From BRA, MGK, Ulverstone, Tasmania.)

an oil that has a different composition from those found in Kenya (Bhakuni et al. 2007). Nevertheless, it is imperative to note that the Tasmanian plantations have dominated the world market because of a thriving breeding program, compared with the East African ones (Li et al. 2011). However, despite the production in different regions of the world, the yield obtained after processing is very small compared with the amounts of dried flowers produced. For instance, 20,000 metric tonnes of dried flowers was observed to give a potential yield of 500 tonnes of 50% pale extract (Glynne-Jones 2001). For this reason, there have also been recent efforts to increase the production by *in vitro* production, although some of these techniques have proved not to be viable because they cannot be used on a large scale (Hitmi et al. 2000).

Owing to the intensive production of this plant in different parts of the world, it is imperative that we critically discuss the pyrethrum plant and the oils extracted from it. Special attention is first given to the botany of the plant. After that, the composition of the oil and its physicochemical properties are evaluated. The general and pesticidal uses are discussed as well, with their merits and demerits highlighted. Finally, an evaluation of the strengths and weaknesses of the analytical and extraction techniques is made.

21.2 Botany of the Plant

Pyrethrum oil is extracted from the dried flowers of the plant *C. cinerariaefolium* (*Tanacetum cinerariaefolium*) (Majoni and Munjanja 2015). The plant, which belongs to the Asteraceae family (Gallo et al. 2017), is small and perennial, with a daisy-like appearance and white petals, and is reported to have originated from Yugoslavia (Wandahwa et al. 1996). The flowering process in the plant is slowed down by low-photon flux density, regardless of temperature. Moreover, high day temperatures of up to 25°C, combined with low-photon flux intensity, have been observed to prevent pyrethrum from flowering in otherwise inductive conditions (Brown and Menary 1994). For this reason, it is grown in highlands of both tropical and subtropical regions of the world, or in lowland regions with temperate climates that induce blooming (Li et al. 2011).

The active ingredients from the pyrethrum flower, which are known as pyrethrins, do not usually exceed 2% of the dry mass (Kiriamiti et al. 2003b). Of this amount, more of it is found in the seed part of the flower than in the flower part. Moreover, when dried, the flower extracts are observed to have a high pyrethrin content (Roncevic et al. 2014). Thus, the drying process carried out before extraction of pyrethrins does not change the pyrethrin content (Morris et al. 2006). However, when a pyrethrum flower is stored for prolonged periods at high temperatures, after harvesting, the pyrethrins may degrade (Atkinson et al. 2004).

21.3 Composition of Oil

The oil, which has insecticidal action, is made up of pyrethrum esters of chrysanthemic acid, and pyrethric acid to three alcohols, namely, pyrethrolone, cinerolone, and jasmololone. This leads to the formation of two fractions commonly known as pyrethrin I (P I), which comprises

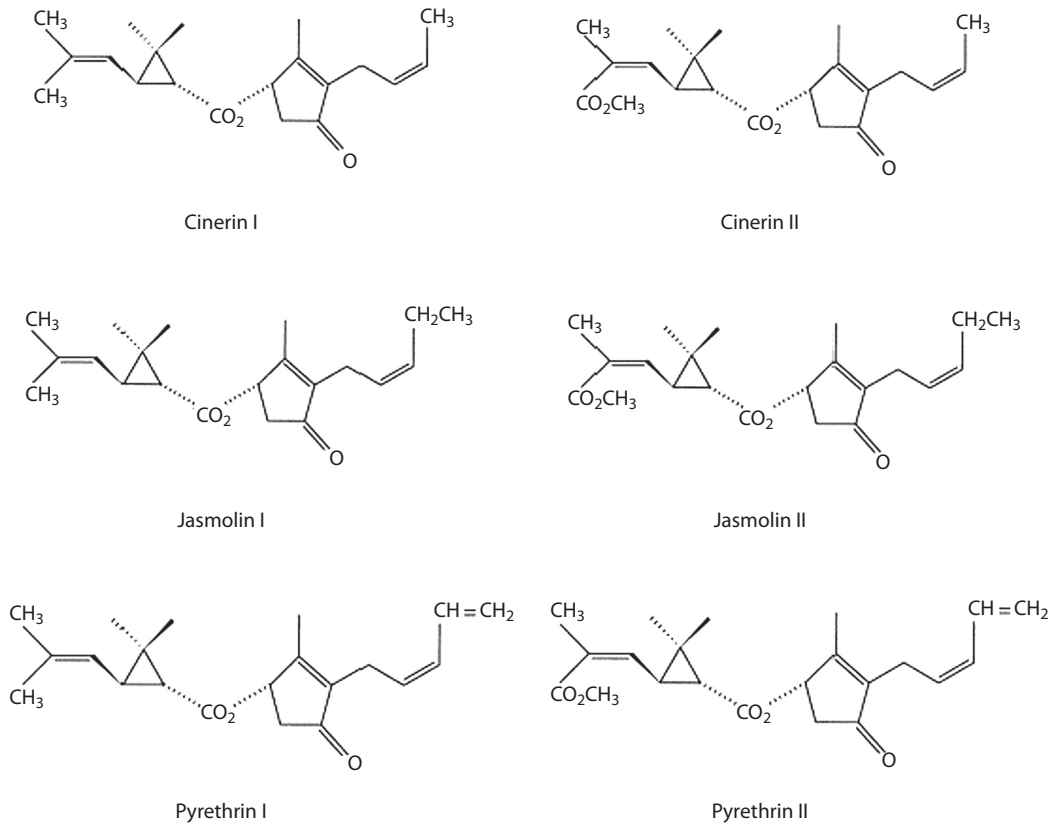

FIGURE 21.2
Structure of pyrethrins. (Reproduced from Henry, C.W. et al., *J. Chromatogr. A*, 863, 89–103, 1999. With permission.)

three esters of chrysanthemic acid: pyrethrin I, cinerin I, and jasmolin I. Pyrethrin II (P II) comprises three esters of pyrethric acid: pyrethrin II, cinerin II, and jasmoline II (Wang et al. 1997). P I compounds have a single ester group, linked to both the tricyclic and pentyl ring systems, differing from each other in the alkene group attached to the five-member ring (Henry et al. 1999). On the other hand, P II compounds have an additional ester moiety attached to the three-member ring, making them more polar than the former. The acid moiety in P I is thought to be formed from D-glucose via 2-C-methyl-D-erytritol 4-phosphate, whereas the alcohol moiety is possibly synthesized from linolenic acid (Matsuda et al. 2005). The relative amounts of the pyrethrins, whose structures are shown in Figure 21.2, depend on factors such as plant genotype, geographical origin and time of harvest, soil conditions, and climate (Li et al. 2014).

21.4 Physicochemical Properties of Oil

The physicochemical properties of pyrethrin oils shown in Table 21.1 may help to explain their behavior in the environment. Generally, pyrethrins are nonpolar and have low

TABLE 21.1

Physicochemical Properties of Pyrethrins

Chemical Compound	Pyrethrin I	Cinerin I	Jasmolin I	Pyrethrin II	Cinerin II	Jasmolin II	Reference
Chemical formula	$C_{21}H_{28}O_3$	$C_{20}H_{28}O_3$	$C_{21}H_{30}O_3$	$C_{22}H_{28}O_5$	$C_{21}H_{28}O_5$	$C_{22}H_{30}O_5$	Head 1973
Molecular weight	328.4	316.4	330.4	372.4	360.4	374.4	Head 1973
Boiling point (°C)	170	136–138	–	200	182–184		Tomlin 2003
Vapor pressure (mmHg)	2.02×10^{-5}	1.1×10^{-6}	4.8×10^{-7}	3.9×10^{-7}	4.6×10^{-7}	1.9×10^{-7}	Tomlin 2003
Water solubility (mg/L)	0.35	3.62	0.60	125.6	1038	214.8	Crosby 1995
K_{ow} (log)	5.62	4.77	5.43	3.56	2.71	3.37	Crosby 1995
BCF	11,000	2,500	4,700	300	70	210	Crosby 1995
Volatilization (μg/cm³/h)	0.89	1.98	1.18	0.65	1.38	1.80	Crosby 1995
Henry's law constant	4.3×10^{-3}	9.4×10^{-4}	3.3×10^{-3}	8.9×10^{-6}	2.2×10^{-6}	1.4×10^{-5}	Crosby 1995

solubility in water (Crosby 1995). P I has lower solubility than P II, as shown by Table 21.1. It also exhibits low volatility, as shown by the low vapor pressures (Tomlin 2003). Finally, the high bioconcentration factors (BCFs) of P I compared with P II can be attributed to their low solubility in water and high octanol–water coefficients. The BCF is a ratio of the concentration of a chemical in an animal to the concentration of that chemical in the environment (Gunasekara 2004).

21.5 General and Pesticidal Uses

Pyrethrin formulations can be in a liquid, dust, or aerosol form, depending on the application. They can be dissolved in water or alcohol, but to increase their toxicity, petroleum is used (Anadon et al. 2009). They find great use in households, where they are used to control human lice, and in mosquito-repellent coils. In addition, they can be used on crops to control insects with great lethality. Applications of their use as veterinary medicines in dogs and cats have also been reported, and they are mainly used as shampoos (Anadon et al. 2009). Finally, they have been reported to be effective against grain weevils (Biebel et al. 2003).

In most of these applications, their efficacy is enhanced by the use of synergists such as piperonyl butoxide (Tomar et al. 1979) and sesamol ethers (Devakumar et al. 1985). Piperonyl butoxide can exist as a synthetic or natural, with some countries preferring the use of the latter to the former in formulations because it is "green" (Cavoski et al. 2011). For instance, piperonyl butoxide synergized pyrethrins were observed to have enhanced activity as grain protectants against four liposcelidid psocids (*Liposcelis bostrychopila* Badonnel, *Liposcelis entomophila* [Enderlein], *Liposcelis decolor* [Pearman], and *Liposcelis paeta*), which were known to be difficult to control in Australia (Nayak 2010).

21.6 Toxicity

Pyrethrin insecticides block the volt-gated sodium channels in nerve axon insects, resulting in a knockdown effect, hyperactivity, and convulsions (Isman 2006). However, the knockdown effect of P I has a lower time than P II. Nonetheless, P II is easily metabolized by insects (Kiriamiti et al. 2003b). For this reason, P I and P II are used synergistically to achieve effective pest control (Winney 1979). A study was carried out to determine the relative toxicities of the pyrethrins to female houseflies (*Musca domestica* L.) (Sawicki et al. 1962). It was found that at 20°C, pyrethrum extract was 1.0; pyrethrin II, 1.3–1.5; pyrethrin I, 0.9–1.0; cinerin II, 0.5–0.6; and cinerin I, 0.4–0.5. In a more recent study, to compare the antifeedent activities of polygodial and pyrethrins against those of white flies (*Bemisia tabaci*) and aphids (*Myzus persicae*), the former was 2–20 times less deterrent than the latter, depending on the insect species (Prota and Bouwmeester 2014). The *Plasmodium falciparum* is the causative agent of malaria, and pyrethrins were also found to have antiplasmodial activity against it, with P II being the most selective antiplasmodial compound (Hata et al. 2011). However, the disadvantage observed with pyrethrins is that some insects are not affected because they render them harmless (Atkinson et al. 2004).

In rats, the toxicity of pyrethrin oils was largely observed to occur by decreasing the ATPase activity by up to 40%, and this was attributed to the presence of piperonyl butoxide (Kakko et al. 2000). Pyrethrin toxicity in humans is very low, although taking large amounts may lead to convulsions (Proudfoot 2005).

21.7 Metabolic Fate

Pyrethrin pesticides have low mammalian toxicity, because they are rapidly metabolized (Majoni and Munjanja 2015). For instance, moderate toxicity was observed for rats (rat oral acute LD_{50} values ranging from 350 to 500 mg/kg). The metabolic pathway in mammals is thought to take place by oxidation of the alcohol and acid moieties of P I. Alternatively, metabolism may take place by hydrolysis of the methyl ester groups (Yamamoto et al. 1969). In rats, cinerin I and jasmoline I were metabolized by hydroxylation of the methyl and methylene groups (Class et al. 1990). In humans, absorption takes place more quickly through the gut than through the skin. Nonetheless, the active components are metabolized rapidly by the liver (Proudfoot 2005).

21.8 Environmental Fate

Despite their advantages, pyrethrins have been replaced by synthetic pyrethroids because of their poor stability in sunlight, reduced efficacy, and high production costs (Katsuda 1999). Pyrethrins degrade in sunlight; for instance, in sunlight the (Z)-pent-2-enyl side chain of the rethrolone moiety changed to the (E)-isomer (Kawano and Yanagihara 1980). However, a study carried out a few years ago showed that the photodegradation of pyrethrins may be slowed down by adding cyclodextrins (Biebel et al. 2003). In another study,

the use of sunscreen agents was reported as a possible alternative to decrease the photodegradation of pyrethrins in formulations (Minello et al. 2005). Pyrethrins were also observed to be degraded in the presence of ultraviolet (UV) light regardless of humidity or the presence of oxygen (Blackith 1952). However, according to another study carried out, the stabilizing effect of piperonyl butoxide to pyrethrins exposed to ultraviolet light was also discovered (Donaldson and Stevenson 1960).

According to another study, temperature is another factor that accelerates the degradation of pyrethrins (Atkinson et al. 2004). This was exemplified by the fact that the pyrethrins decreased by 26%, 65%, and 68%, respectively, as the temperature increased from 20°C to 60°C and finally 100°C. The authors suggested that the concentration did not reach zero because of the plant structure.

The fate of pyrethrins in plants has been studied intensively by many authors, who have shown that they degrade quickly. For instance, a recent study showed that the half-lives of pyrethrins on field-grown tomatoes and bell pepper fruits did not exceed 2 hours (Antonius 2004). In another field experiment, the fate of pyrethrins in peaches was investigated, and the half-life of P I was found to be 2.3 days, and that of P II 6.6 days (Angioni et al. 2005). It is important to note that the half-lives increased in formulations where piperonyl butoxide was used. Moreover, the findings from both studies corroborate the fact that pyrethrins degrade quickly under field conditions, especially when light is present. In contrast, the absence of sunlight was shown to decrease the degradation rate of pyrethrins. This is exemplified by a study carried out to determine the degradation of pyrethrin residues on stored durum wheat after postharvest treatment. It was found that in the absence of light, pyrethrins were stable for 22 days and took 8 months to dissipate completely (Caboni et al. 2007).

Residues of pyrethrins on potato leaves and in soil under field conditions were also determined using high-performance liquid chromatography (HPLC) coupled to UV detection. Residues of pyrethrin I in compost treatments (0.056 μg/g) were higher than in no-mulch treatments (0.026 μg/g) (Antonius et al. 2001). In addition, P I bound more strongly to soils because it has a very large K_{oc}.

Concentrations of pyrethrins on an average of 36.1 ng/L have been reported in runoff water after they had been applied 11 days in advance (Antonius et al. 1997). In a separate study carried out, pyrethrins were detected in surface waters collected from five tributaries of the San Francisco Bay, California, at concentrations of less than 8.96 ng/L (Woudneh and Oros 2006).

21.9 Methods of Extraction

Pyrethrins are extracted from pyrethrum flowers to obtain oleoresin, which contains pyrethrum I and II as the major components; other chemical components found in the extracts include carotenoids, sesquiterpenes, sesquiterpenoid lactones, flavonoids, n-alkanes, and various fatty acids (Casida 1973; Head 1973). These components can give rise to possible interference during analysis (Head 1968). For this reason, extraction techniques should produce an extract with high recovery of pyrethrin esters. The recovery rate may depend on the solvent used; for instance, nonpolar solvents like hexane give a very high content of total pyrethrins in the final extract (Nagar et al. 2015). Examples of techniques that have been used to extract pyrethrins include ultrasonic extraction (USE), Soxhlet extraction,

and supercritical fluid extraction (SFE) (Otterbach and Wenclawiak 1999). A similarity between Soxhlet extraction and USE is that both of them use energy, which facilitates the continuous extraction of analytes by mass transfer, and thus the analyte leaches out in two successive elutions (Nagar et al. 2015). Other methods that have been used are maceration in a solvent such as n-hexane and cyclically pressurized extraction, also known as rapid solid–liquid dynamic extraction (RSDLE) (Gallo et al. 2017).

21.9.1 Soxhlet Extraction

Soxhlet extraction involves placing the sample in an extractor, and subsequently distilling, while introducing fresh portions of solvent at intervals (Turiel and Martin-Esteban 2008). The advantage of this technique is that good extraction results are obtained because the extraction solvent is recycled continuously at high temperatures (Nagar et al. 2015).

In an early study that was carried out to explore the possibility of using Soxhlet extraction for extraction of pyrethrin oils from pyrethrum flowers, it was observed that use of a warm solvent gave erroneous results for P II. On the other hand, cold extraction gave low values of P II, and it eliminated the variations that were obtained with different grades of ligroin (Mitchell and Tresadern 1949). The amount of pyrethrins extracted using this technique also depends on the solvent used. For instance, acetonitrile gave the best results in a recent study carried out (Nagar et al. 2015).

21.9.2 Supercritical Fluid Extraction

Supercritical fluid extraction involves the use of a supercritical fluid such as carbon dioxide to extract solid samples. The advantage of using a supercritical fluid is that extraction of analytes is possible even in pores that are not easily accessible (Turiel and Martin-Esteban 2008). In addition, it can be coupled to gas chromatography (GC) (Wenclawiak and Otterbach 2000) or HPLC. The coupling of SFE to these chromatographic techniques offers extraction of unlimited sample volumes (Pol and Wenclawiak 2003). The variables that affect the extraction efficiency include pressure, temperature, and particle size (Kiriamiti et al. 2003b). Other advantages include being environmentally friendly because of the absence of solvents. Notwithstanding the above advantages, SFE is very expensive, and it is not universally applicable (Gallo et al. 2017).

A method was developed to extract P I and P II from pyrethrum flower, and the extraction efficiencies under various conditions were examined (Pan et al. 1995). It was found that the most effective extractions of P I and P II were at 40°C and 1200 psi. In addition, the extraction efficiencies of the technique were better than those obtained with n-hexane. However, this is in contrast to a more recent study that was carried out to explore the supercritical fluid extraction of pyrethrins from pyrethrum flowers, where the extract was similar to that obtained using hexane in terms of waxes and oils (Kiriamiti et al. 2003b). Notwithstanding the above fact, the same research group improved the quality of the extract by carrying out the fractionation in two steps (Kiriamiti et al. 2006). However, the ideal was not reached because the separators were too small. In another study, the same research group showed that supercritical carbon dioxide can be used to purify oleoresin that had been previously extracted with hexane (Kiriamiti et al. 2003a). The extract obtained was of high quality and contained a high concentration of pyrethrins.

Studies have been carried out to compare SFE with other extraction techniques, such as USE and Soxhlet extraction (Otterbach and Wenclawiak 1999). Both studies have shown that the quality of the extract was better than that of USE. Recently, the technique has also

been compared with maceration and cyclic pressurized extraction, and the extraction efficiency was comparable to that of the other techniques (Gallo et al. 2017).

21.9.3 Ultrasonic Extraction

USE makes use of mechanical waves to alter the physical and chemical properties of a matrix by cavitations, thus releasing the extractant from the matrix (Luque-Garcia and Luque de Castro 2003). Sonication is usually carried out in a sonication bath or sonication probes (Fenoll et al. 2011).

A study was carried out to compare the extraction efficiency of four extraction techniques: percolation, agitation with heat, Soxhlet extraction, and USE. It was discovered that energy-assisted extraction techniques like agitation and USE increased the extractive yield by 20%–50% (Nagar et al. 2015). Moreover, the best results for sonication were found using acetonitrile as the extraction solvent.

21.10 Methods of Analysis

21.10.1 Supercritical Fluid Chromatography

Supercritical fluid chromatography (SFC) uses a supercritical fluid such as carbon dioxide as the mobile phase. This gives it a competitive edge over other chromatographic techniques because it is fast, environmentally friendly, and highly efficient (El-Saeid and Khan 2010). Factors affecting chromatographic separation efficiency in SFC include pressure gradients, density, and temperature (Wenclawiak et al. 1998). Another important thing to consider before analysis can be done is calibration. However, this may not always be problematic. Hence, allethrin can be used as a reference standard because it has a structure that is similar to that of the compounds (Wenclawiak and Otterbach 2000).

SFC with positive pressure and negative temperature gradients was successfully used to separate pyrethrins (Wenclawiak et al. 1998).

21.10.2 Gas Chromatography

Gas chromatography is used to analyze analytes that can be volatilized by coupling to a selective detector such as a flame ionization detector (FID) (Class 1991) or electron capture detector (ECD) (Berger-Preib et al. 1997). Gas chromatographic methods have been used for a long time to analyze pyrethrum extracts with great precision (Kawano et al. 1974). A study revealed that use of shorter columns and a thinner stationary phase is not sufficient to eliminate degradation of pyrethrins (Wieboldt et al. 1989). It is of paramount importance to note that when carrying out the analyses of pyrethrins, elution temperatures should not exceed 200°C, because hot injection ports cause tautomerization of P I and P II and poor peak shapes (Wieboldt et al. 1989). GC analysis using a temperature less than 210°C was successfully used to separate pyrethrins without any degradation (Class 1991).

A trend observed is the use of gas chromatography–mass spectrometry (GC-MS) to separate, quantify, and identify the pyrethrins (Wenclawiak et al. 1997; Cai et al. 2013). GC-MS coupled to SFE at high temperature and a catalyst was used to quantify and identify the pyrethrin esters, with high quantitative conversion (Wenclawiak et al. 1997). In a

recent study, GC-MS was successfully used to determine the amounts of the chemical compounds in flower extracts, by use of peak area normalization (Cai et al. 2013).

Despite the usefulness of GC-based methods in the separation and quantitation of pyrethrins, their use has decreased over the years because pyrethrins degrade at high temperatures. For this reason, HPLC-based methods can be used.

21.10.3 High-Performance Liquid Chromatography

Normal phase high-performance liquid chromatography (NP-HPLC) involves the use of a stationary phase that is more polar than the mobile phase. In an earlier study, NP-HPLC was used to separate the pyrethrin esters at 229 nm, with some interference from UV-absorbing material in the extract (McEldowney and Menary 1988). However, in a more recent study NP-HPLC was successfully used to quantify the components of pyrethrum extract, without any interference from the sample matrix (Essig and Zhao 2001a). The same research group separated and characterized pyrethrum extract standard by semipreparative NP-HPLC, obtaining an assay content that was close to that reported by the AOAC International titration method (Essig and Zhao 2001b).

Reverse phase high-performance liquid chromatography (RP-HPLC), which relies on nonpolar stationary phases such as C18 and C8 (Botitsi et al. 2011), can be used to separate and purify pyrethrum extracts (Wei et al. 2006). A study was carried out to determine pyrethrins in pyrethrum extracts by RP-HPLC with diode array detection at 240 nm (Wang et al. 1997). Well-resolved peaks were obtained at 240 nm, as shown by Figure 21.3. Changing the wavelength to 230 nm gave poor resolution between cinerin I and pyrethrin I. In another study, different stationary phases were compared for the separation efficiency using RP-HPLC (Nagar et al. 2015). It was found that the C18 column (3.9 × 150 mm, 5 μm) resolved the pyrethrin mixtures well with great sensitivity, as shown by Figure 21.4.

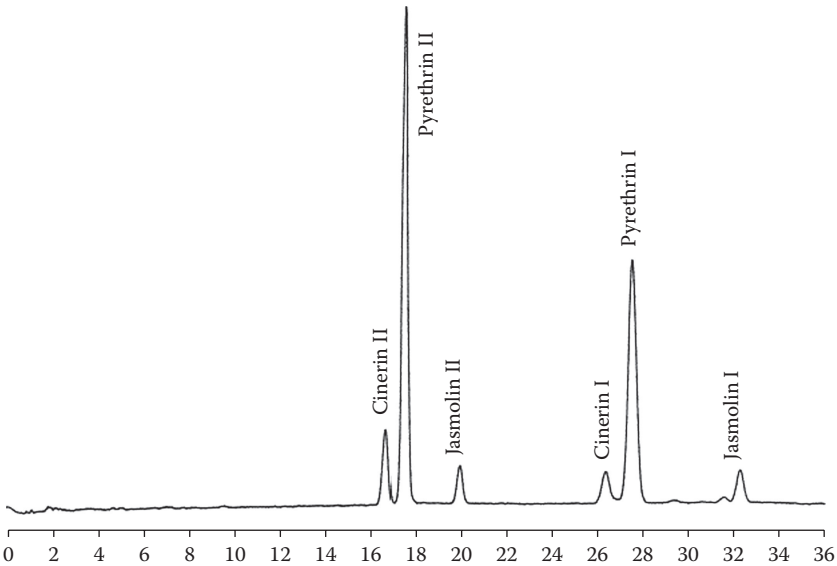

FIGURE 21.3
Reverse phase HPLC chromatogram of pyrethrum extract. (Reproduced from Wang, I. et al., *J. Chromatogr. A*, 766, 277–281, 1997. With permission.)

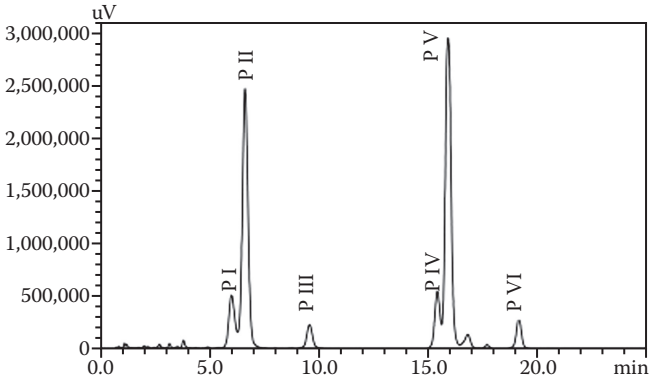

FIGURE 21.4
HPLC chromatogram of standard pyrethrins. P I, cinerin II; P II, pyrethrin II; P III, jasmolin II; P IV, cinerin I; P V, pyrethrin; P VI, jasmolin I. (Reproduced from Nagar, A. et al., *Ind. Crops Prod.*, 76, 955–960, 2015. With permission.)

A recent advancement in HPLC is the use of ultra-high-performance liquid chromatography (UHPLC), which has reduced particle size and higher flow rates for increased speed, with improved resolution and signal-to-noise ratio (Leandro et al. 2006). UHPLC with photodiode array detection and aerosol detection was used to detect pyrethrins with great sensitivity and precision (Thomas et al. 2015).

Another recent advance is the use of nanoliquid chromatography, which utilizes flow rates of nanoliters per minute, and therefore provides high sensitivity because of lower chromatographic dilution and higher efficiency (Asimakopoulos et al. 2015). This technique has previously been used in the analysis of synthetic pesticides using various stationary phases (Cappielo et al. 2003; Buonasera et al. 2009). Recently, reverse phase nanoliquid chromatography coupled to direct electron ionization–mass spectrometry (nanoLC–direct EI MS) was successfully used to detect and quantify pyrethrins in pyrethrum extracts with high sensitivity and precision (Cappielo et al. 2012).

21.10.4 High-Performance Capillary Electrophoresis

The pyrethrin esters were separated using micellar electrokinetic chromatography (MEKC) by comparing two pseudostationary phases, namely, sodium dodecyl sulfate (SDS) and polymeric sodium N-undecyl sulfate (poly-SUS) (Henry et al. 1999). The advantage of this technique over HPLC is the shorter analysis times obtained for both pseudostationary phases. However, the use of a pseudostationary phase can be a problem. Hence, other techniques that use a stationary phase, such as capillary electrochromatography (CEC), can be explored.

21.10.5 Capillary Electrochromatography

Capillary electrochromatography is a technique that separates analytes between the mobile and stationary phases by electro-osmotic flow (Dittman and Rozing 1996). CEC was successfully used to separate six pyrethrin esters with reduced runtimes of up to 16 minutes (Henry et al. 2001). However, according to the study, the technique shows low sensitivity for pyrethrins that are in low concentration. This may require an additional concentration step.

21.11 Conclusions

There is now ample evidence to prove that the continuous use of synthetic pesticides leads to environmental degradation. Hence, the use of plant-based pesticides, which are environmentally friendly, has been explored. The pyrethrins derived from the pyrethrum plant, apart from being environmentally friendly are very effective as insecticides, producing a rapid knockdown effect. Another distinct advantage is that they are readily metabolized in mammals such as rats and humans, only causing toxicity if taken in large amounts.

However, they also have a major disadvantage of rapidly degrading in the presence of sunlight. Synergists and sunscreen agents have been successfully used to improve their half-lives under field conditions. For this reason, they remain one of the most effective plant-based insecticides.

It is worth mentioning that numerous advances have been made in both extraction and analysis techniques. Extraction techniques have evolved from laborious techniques such as Soxhlet extraction, which require large amounts of organic solvents, to the use of green techniques such as SFE, which have high recoveries. In addition, chromatographic techniques have been successfully used to separate and quantify the pyrethrins in extract, with good sensitivity and precision. A notable improvement is the use of mass spectrometry to identify the individual pyrethrins without any interference.

In conclusion, much research has been published on pyrethrin-related topics such as extraction and analysis techniques, and metabolic and environmental fate. Moreover, the use of stabilizers and synergists to increase their photostability is remarkable, and this may lead to their continued use. However, in terms of efficacy, they may not exactly match the synthetic pesticides.

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