Natural Product Research: Formerly Natural Product Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gnpl20

Synthesis and insect attractant activity of fluorine-containing Pinus diterpenic amides and imines

Xiaoping Rao [a] , Zhanqian Song [a] , Zhaojiu Han [b] & Zhikuan Jiang [b]
[a] Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing, P.R. China
[b] Military Medicine Institute of Nanjing Command, Nanjing, P.R. China
Published online: 29 Oct 2009.

To cite this article: Xiaoping Rao , Zhanqian Song , Zhaojiu Han & Zhikuan Jiang (2009): Synthesis and insect attractant activity of fluorine-containing Pinus diterpenic amides and imines, Natural Product Research: Formerly Natural Product Letters, 23:9, 851-860

To link to this article: http://dx.doi.org/10.1080/14786410802155954

Natural Product Research
Vol. 23, No. 9, 15 June 2009, 851–860

Taylor & Francis
Taylor & Francis Group

Synthesis and insect attractant activity of fluorine-containing *Pinus* diterpenic amides and imines

Xiaoping Rao[a]*, Zhanqian Song[a], Zhaojiu Han[b] and Zhikuan Jiang[b]

[a]*Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing, P.R. China;* [b]*Military Medicine Institute of Nanjing Command, Nanjing, P.R. China*

(*Received 17 October 2007; final version received 23 April 2008*)

A series of fluorine-containing *Pinus* diterpenic amides and imines have been synthesised and their structures were confirmed by elemental analysis, IR, ^{1}H NMR spectroscopy and single crystal X-ray diffraction. Their insect attractant activity to *Spodoptera litura* were screened by leaf plate method; the results indicated that most fluorine-containing dehydroabietic amides and imines exhibited attractive activity to *S. litura*, in which dehydroabietic *p*-trifluoromethyl amide (**A6**) exhibit seven times the attractive rate compared with blank at the concentration of $0.01\,g\,mL^{-1}$. The fluorine moiety fused to the benzene ring results in decreased attractive rates for amides except (**A6**), while the effects of fluorine result in increased attractive rates for diterpenic imines.

Keywords: fluorine-containing *Pinus* diterpenic; single crystal; insect attractant; attractive rate

1. Introduction

Insect attractants are useful chemicals for determining movement of insect populations; they are used in an environmentally friendly way that has no negative effect on other animals or humans (Hao, Thi, Giang, Khoa, & Son, 1996). The most common use of chemical attractants is in traps, to monitor insect populations, and they can also be widely used as poison bait to disrupt insect mating. Insect attractants and feeding arrestants are usually used in combination with an insecticide in pest management programmes (Momin & Nair, 2002). *Spodoptera litura* is a widely dispersed pest in Asia and Pacific regions, and is also a polyphagous pest for many agricultural crops. They will chew large areas of the leaf and even can defoliate a crop when the pests are numerous. In such cases, the larvae migrate in large groups from one field to another in search of food. So, to prevent and control *S. litura* is of great importance to agriculture in these areas.

Developing high value products from main chemical components of natural resources through chemical modification is an important direction of natural product research. *Pinus* diterpenic resin acids have attracted great interest for their special chemical structures and wide range of biological activities. The major component of disproportionated rosin – dehydroabietic acid – is extremely stable to air oxidation, so that it is suitable

*Corresponding author. Email: rxping2001@163.com

ISSN 1478–6419 print/ISSN 1029–2349 online

DOI: 10.1080/14786410802155954
http://www.informaworld.com

as a raw material for design and synthesis of biological derivatives (Kushnir et al., 2003). The derivatives of diterpenic resin acids displayed a significant series of biological activities, such as anti-bacterial, anti-fungal, anti-cancer and anti-inflammatory (Feio, Gigante, Roseiro, & Marcelo-Curto, 1999; Feio, Roseiro, Gigante, & Marcelo-Curto, 1997; San, Gordaliza, Salinero, & Miguel, 1993; Smith, Williamson, Zloh, & Gibbons, 2005; Ulusu, Ercil, Sakar, & Tezcan, 2002; Wada et al., 1985; Yanez, Theoduloz, & Schmeda-Hirschmann, 2005). Naturally occurring resin acids have insect anti-feedant characteristics; isopimaric acid is superior to other resin acids in inhibiting *larval* development in several *Lepidoptera* species, including the pink bollworm.

It is well known that fluorine can affect the biological activities of compounds in a number of ways due to its unique properties, such as high thermal stability, lipophilicity, special biomimetic effect and electronegativity (Xua, Qianb, Lia, Songa, & Chena, 2005). This implied that introducing fluorine atoms into the parent compound could cause a big change in its bioactivities.

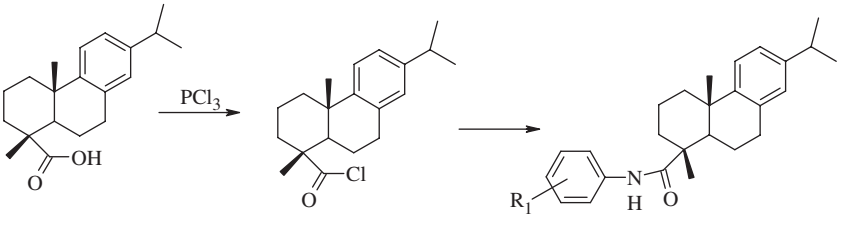
Although much attention has been paid to the biological derivatives of dehydroabietic acid, its fluorine-containing derivatives have not yet been dealt with. In this article, we describe the synthesis and insect attractant activity of fluorine-containing *Pinus* diterpenic amides and imines.

2. Results and discussion

2.1. *Synthesis*

The tricyclic phenanthrene structure of dehydroabietic acid has high sterical hindrence to the carboxyl acid group; the modification of the carboxyl acid needs secure conditions, such as high temperature, high pressure and a catalyst (Kushnir et al., 2003). However, the reaction activities can be highly promoted through a chloride intermediate. Trichloro phosphorous has been found to be the best reagent to prepare dehydroabietic chloride. Fluorine-containing dehydroabietic amides can be obtained from dehydroabietic acid through chloride intermediate by two steps of reactions. The reaction process is shown in Scheme 1.

Fluorine-containing dehydroabietic imines can be obtained by direct condensation reaction with dehydroabietylamine and fluorine-containing benzaldehydes. Despite of sterical hindrance to the amino group of tricyclic phenethrane structure, the condensation reaction affords high yields of fluorine-containing imines. Scheme 2 shows the reaction process of fluorine-containing dehydroabietic imines.



Comp	A1	A2	A3	A4	A5	A6
R_1=	H	*o*-F	*p*-F	2,6-F	3,5-F	*p*-CF3

Scheme 1. Reaction process of fluorine-containing amides.

*Dehydroabietic anilide (**A1**)*: $C_{26}H_{33}NO$, white crystal: yield 69.8%, m.p. 139.2°C, elemental analysis: calculate(found),C: 83.20(83.21); H: 8.80(8.78); N: 3.73(3.70); IR(cm^{-1}): 3339(N–H); 2956(–CH_3,–CH_2); 1659(O=C–N); 823(Ar–H); ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 7.56(1H,CONH–); 7.54–6.91 (8H, C=CH–); 2.86(1H, $-CH(Me)_2$); 2.93–1.61(10H, $-CH_2-$); 1.63 (1H, >CH–); 1.43–1.24(12H, $-CH_3$).

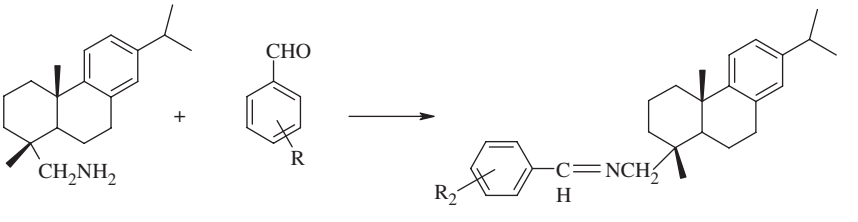
*Dehydroabietic o-fluoro-anilide (**A2**)*: $C_{26}H_{3I3}NO$, white crystal: yield 58.5%, m.p. 93.2°C, elemental analysis: calculate(found), C: 79.39(79.27); H: 8.14(8.19); N: 3.56(3.52); IR(cm^{-1}): 3316(N–H); 2960(–CH_3,–CH_2); 1654(O=C–N); 821(Ar–H); ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 7.80 (1H, CONH–); 8.36–6.91 (7H, C=CH–); 2.86 (1H, –$CH(Me)_2$); 2.93–1.64 (10H, $-CH_2-$); 1.61 (1H, >CH–); 1.46–1.25 (12H, $-CH_3$).

*Dehydroabietic p-fluoro-anilide (**A3**)*: $C_{26}H_{3I3}NO$, white crystal: yield 46.3%, m.p. 141.1°C, elemental analysis: calculate(found), C: 79.39(79.43); H: 8.14(8.07); N: 3.56(3.52); IR(cm^{-1}): 3423(N–H); 2955(–CH_3,–CH_2); 1659(O=C–N); 831(Ar–H); ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 7.80 (1H, CONH–); 7.22(1H, CONH–); 7.50–6.90(7H, C=CH–); 2.85(1H, –$CH(Me)_2$); 2.92–1.80(10H, $-CH_2-$); 1.59(1H, >CH–); 1.42–1.24(12H, $-CH_3$).

*Dehydroabietic 2,6-difluoro-anilide (**A4**)*: $C_{26}H_{31}F_2NO$, white crystal: yield 58.6%, m.p. 159.9°C, elemental analysis: calculate(found), C: 75.91(75.88); H: 7.54(7.50); N: 3.41(3.44); IR(cm^{-1}): 3310(N–H); 2960(–CH_3,–CH_2); 1659(O=C–N); 826(Ar–H); ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 7.27(1H, CONH–); 7.22–6.91(6H, C=CH–); 2.85(1H, –$CH(Me)_2$); 2.94–1.78 (10H, $-CH_2-$); 1.56(1H, >CH–); 1.44–1.24(12H, $-CH_3$).

*Dehydroabietic 3,5-fifluoro-anilide (**A5**)*: $C_{26}H_{31}F_2NO$, white crystal: yield 56.9%, m.p. 134.1°C, elemental analysis: calculate(found), C: 75.91(75.96); H: 7.54(7.56); N: 3.41(3.40); IR(cm^{-1}): 3315(N–H); 2961(–CH_3,–CH_2); 1644(O=C–N); 805(Ar–H); ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 7.85(1H, CONH–); 7.44–6.77(6H, C=CH–); 2.85(1H, –$CH(Me)_2$); 2.92–1.80 (10H, $-CH_2-$); 1.62(1H, >CH–); 1.45–1.23(12H, $-CH_3$).

*Dehydroabietic p-trifluoromethyl-anilide (**A6**)*: $C_{27}H_{3I33}NO$, white crystal: yield 43.3%, m.p. 169.5°C, elemental analysis: calculate(found), C: 73.14(73.20); H: 7.22(7.16); N: 3.16(3.22); IR(cm^{-1}): 3341(N–H); 2961(–CH_3,–CH_2); 1675(O=C–N); 841(Ar–H); ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 7.69(1H,CONH–); 7.67–6.90(6H,C=CH–); 2.89(1H,–$CH(Me)_2$); 2.92–1.80 (10H, $-CH_2-$); 1.59(1H, >CH–); 1.43–1.23(12H, $-CH_3$).



Comp	I1	I2	I3
R_2=	H	*m*-F	*p*-CF_3

Scheme 2. Reaction process of fluorine-containing imines.

*Dehydroabietylamine benzaldehyde imine (**I1**)*: $C_{27}H_{35}N$, white crystal: yield 70.2%, m.p. 104.5°C, elemental analysis: calculate(found), C: 86.22(86.86); H: 9.49(9.39); N: 3.61(3.75), IR(cm^{-1}): 2931(–CH_3,–CH_2); 1644(C=N); 1040(C–N); 832(Ar–H),^{1}H NMR: ($CDCl_3$. δ/ppm. 400 MHz), 8.26(1H, N=C<u>H</u>–); 7.76–6.91(8H, C=C<u>H</u>–); 3.54(2H, N–C<u>H_2</u>–); 2.88(1H, –C<u>H</u>$(Me)_2$); 2.86–1.58(10H, –C<u>H_2</u>–); 1.27–1.08(12H, –C<u>H_3</u>).

*Dehydroabietylamine m-fluoro-benzaldehyde imine (**I2**)*: $C_{27}H_{34}FN$, white crystal: yield 95.3%, m.p. 89.2°C, elemental analysis: calculate(found), C: 83.26(83.16); H: 8.77(8.69); N: 3.41(3.58), IR(cm^{-1}): 2930(–CH_3,–CH_2); 1654(C=N); 1134(C–N); 785(Ar–H), ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 8.24(1H, N=C<u>H</u>–); 7.51–6.91(7H, C=C<u>H</u>–); 3.53(2H, N–C<u>H_2</u>–); 2.91(1H, –C<u>H</u>$(Me)_2$); 2.85–1.56(10H, –C<u>H_2</u>–); 1.28–1.09(12H, –C<u>H_3</u>).

*Dehydroabietylamine p-trifluoromethyl benzaldehyde imine (**I3**)*: $C_{28}H_{34}F_3N$, white crystal: yield 86.9%, m.p. 119.5°C, elemental analysis: calculate(found), C: 75.97(76.19); H: 7.71(7.71); N: 3.21(3.17), IR(cm^{-1}): 2930(–CH_3,–CH_2); 1654(C=N); 1134(C–N); 785(Ar–H), ^{1}H NMR: ($CDCl_3$ δ/ppm. 400 MHz), 8.24(1H, N=C<u>H</u>–); 7.51–6.91 (7H, C=C<u>H</u>–); 3.53(2H, N–C<u>H_2</u>–); 2.91(1H, –C<u>H</u>$(Me)_2$); 2.85–1.56(10H, –C<u>H_2</u>–); 1.28–1.09(12H, –C<u>H_3</u>).

2.2. *X-ray single crystal structure*

White crystals suitable for X-ray analysis were obtained by solvent evaporation under room temperature. The crystallographic details are summarised in Table 1. The selected bond lengths and angles are shown in Table 2.

As shown in Figure 1, the two crystallographically independent molecules in the crystal structure of compound **I2**, in each molecule there are four six-membered rings which exhibited plane, half-chair, chair and plane configurations, respectively. (The atomic coordinates, bond lengths and angles and the X-ray crystallographic files on CIF format for the determination of compound **I2** can be obtained from the author by request). The two methyl groups on the phenanthrene structure were in the same side of rings. There are two fluorine atoms in each molecules, the atom occupational rate is 50%, respectively. The atoms of isopropyl group showed disorder. The bond lengths of C=N and C–N were 1.268 Å and 1.433 Å, respectively. C=N bond exhibited *trans* configuration. The packing diagram of compound **I2** is shown in Figure 2; hydrogen bond and weak $\pi\cdots\pi$ stack make the molecules stable.

2.3. *Insect attractant activity*

The insect attractant activity of fluorine-containing dehydroabietic amides and imines to *S. litura* were investigated at the concentration of 0.01 g mL^{-1}. The attractive rates of compounds at 24, 48 and 72 h are listed in Table 3, 4 and 5, respectively. These data are summarised in Table 6. The bigger attractive rate means the attractant activity is higher. The results below zero mean the compounds exhibited anti-feedant activity to *S. litura*.

At the first 24 h bioassay, some fluorine-containing amides exhibited higher attractive rates and some displayed lower attractive rates compared with parent compound. All fluorine-containing imines exhibited higher attractive rates compared with parent compound. After 48 h bioassay, most fluorine-containing compounds except for **A6** exhibited lower attractive rates while all imines exhibited higher attractive rates compared

Table 1. Crystal data and structure refinement for **I2**.

Empirical formula	$C_{27}H_{30}FN$
Formula weight	387.52
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P2_1$
a (Å)	6.0280 (12)
b (Å)	10.996 (2)
c (Å)	18.519 (4)
α (°)	74.20 (3)
β (°)	82.29 (3)
γ (°)	77.01 (3)
V (Å^3)	1147.4 (4)
Density (calculated) (mg m^{-3})	1.122
Absorption coefficient (mm^{-1})	0.070
F(0 0 0)	416
Crystal size (mm^3)	$0.30 \times 0.20 \times 0.10$
θ range for data collection (°)	1.96 to 25
Limiting indices	$0 \le h \le 7$, $-12 \le k \le 13$, $-21 \le l \le 22$
Reflections collected/unique	4365/4365
Completeness to $\theta = 25.99$ (%)	98.4
Max. and min. transmission	0.9821, 0.9309
Data/restraints/parameters	4365/3/559
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0961$, $wR_2 = 0.2772$
R indices (all data)	$R_1 = 0.1608$, $wR_2 = 0.2262$
Absolute structure parameter	2(4)
Largest diff. peak and hole (e Å^{-3})	0.363, −0.184

Note: $R_1 = \sum \|F_0| - |F_c\| / \sum |F_0|$; $wR_2 = \sum[w(F_0^2 - F_c^2)^2 / \sum[w(F_0^2)^2]^{1/2}$.

with parent compound. After 72 h bioassay, most fluorine-containing compounds except for **A6** and **A2** exhibited lower attractive rates, while most imines except for **I3** exhibited higher attractive rates compared with parent compound.

The attractive rates of all diterpenic fluorine-containing compounds to *S. litura* are listed in Table 6. From the results, it can be concluded that the fluorine atom introduced to the amides may result in the decrease of attractive rates of dehydroabietic amides except **A6**, while the introduction of fluorine atom to the imines may lead to the increase of attractive rates of dehydroabietic imines. The trifluoromethyl amide and *m*-fluoro imine exhibited higher activities than that of parent compound by four to seven times in terms of attractive rates. These compounds exhibited higher attractant activities at the first 24 h bioassay, the activities are higher at first, after 48 h the activity reduced greatly, and at 72 h the activities increased.

3. Experimental

3.1. *Reagents and instruments*

All chemicals purchased were of reagent grade and used without further purification. Infrared spectrum was recorded as KBr pellets on a Bio-Rad FTS-185

Table 2. Selected bond lengths and angles for **I2**.

Bond length (Å)	
N(1)–C(19)	1.268 (11)
N(1)–C(18)	1.433 (11)
C(7)–C(6)	1.377 (12)
N(2)–C(33)	1.232 (11)
N(2)–C(34)	1.460 (11)
C(41)–C(42)	1.530 (12)
F(1)–C(24)	1.241 (15)
F(2)–C(22)	1.23 (2)
Bond angles (°)	
C(3)–C(2)–C(4)	112.7 (10)
C(6)–C(7)–C(9)	121.9 (7)
C(19)–N(1)–C(18)	120.0 (8)
C(29)–C(30)–C(31)	119.5 (9)
F(1)–C(24)–C(23)	119.8 (15)
F(2)–C(22)–C(21)	122.6 (15)
N(1)–C(18)–C(17)	112.4 (7)
F(3)–C(28)–C(29)	124.7 (16)
C(48)–C(47)–C(46)	120.0 (11)
Torison angles (°)	
C(16)–C(15)–C(14)–C(9)	56.7 (9)
C(24)–C(23)–C(22)–F(2)	169.8 (18)
C(24)–C(23)–C(22)–C(21)	1 (2)
C(10)–C(11)–C(12)–C(6)	−42.5 (11)
N(1)–C(19)–C(20)–C(25)	170.3 (10)
C(16)–C(17)–C(18)–N(1)	50.7 (9)
C(54)–C(17)–C(18)–N(1)	−70.3 (9)
C(40)–C(39)–C(38)–C(37)	56.3 (10)
C(37)–C(35)–C(41)–C(40)	−50.4 (8)
C(44)–C(49)–C(48)–C(50)	179.6 (10)

IR spectrophotometer. Melting points were determined by XT5 melting point apparatus. ^{1}H NMR spectrum was recorded on a Bruker AVANCE 400 spectrometer. ($CDCl_3$ as solvent). C, H, N elemental analysis was performed by a PE-2400CHN instrument.

3.2. *Synthesis of dehydroabietic amides*

A mixture of dehydroabietic acid (0.1 mol), phosphorous trichloride (6 mL) and chloroform (40 mL) was stirred at 333 k for 3 h, then trichloroform was distilled off and the residue was added to the fluorine-containing aniline (0.2 mol) in toluene solution; after further 24 h stirring at room temperature, the resulting mixture was filtrated and the filter was washed with hydrochloride and water, then the solvent was distilled off, upon recrystallisation from acetone, white crystals were obtained.

3.3. *Synthesis of dehydroabietic imines*

The dehydroabietic imines were prepared according to the procedure of direct condensation reaction. Dehydroabietylamine (10 mmol) dissolved in 200 mL ethanol,

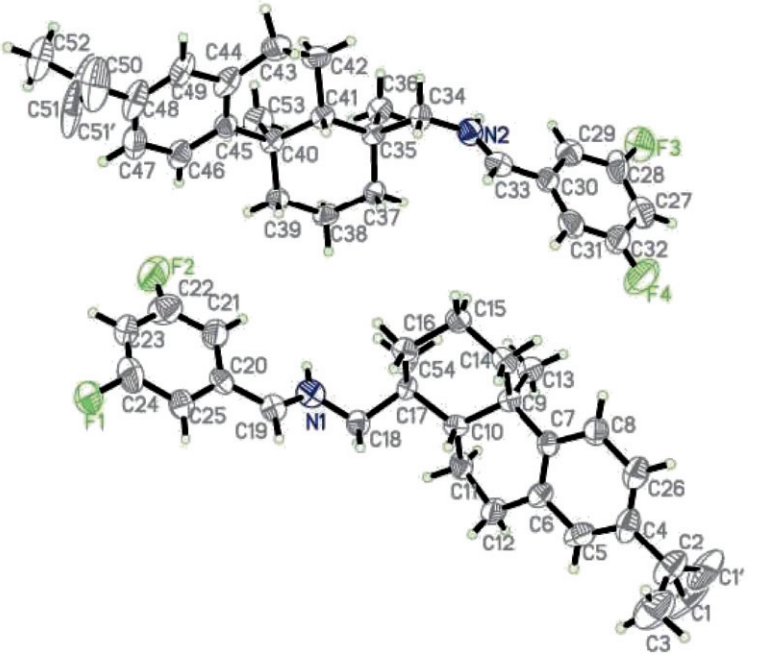


Figure 1. ORTEP diagram of crystal **I2**.

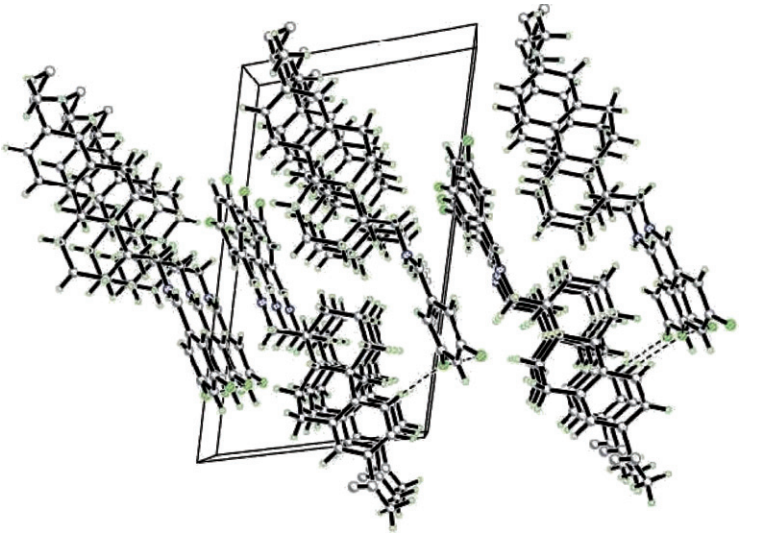


Figure 2. Molecular packing arrangement in the unit cell of crystal **I2**.

10 mmol fluorine-containing benzaldehyde dissolved in 100 mL ethanol solution were added dropwise into the dehydroabietylamine solution, the mixture were refluxed for 3 h and the crystal was filtrated and recrystallised from acetone. Single crystals were grown from acetone.

Table 3. Attractive rates of dehydroabietic amides and imines to *Spodoptera litura* after 24 h.

Compound	Times of medcine	Times of blank	Attractive rate (%)
A1	67	22	206.67
A2	40	18	122.22
A3	15	18	−16.67
A4	3	15	−80.00
A5	19	30	−36.67
A6	58	8	650.00
I1	15	51	−70.59
I2	36	9	300.00
I3	57	21	171.43

Table 4. Attractive rates of dehydroabietic amides and imines to *Spodoptera litura* after 48 h.

Compound	Times of medcine	Times of blank	Attractive rate (%)
A1	341	220	38.14
A2	52	51	1.96
A3	56	46	21.74
A4	37	41	−9.76
A5	53	61	−13.12
A6	141	46	206.52
I1	170	114	49.12
I2	181	59	206.78
I3	233	136	71.32

Table 5. Attractive rates of dehydroabietic amides and imines to *Spodoptera litura* after 72 h.

Compound	Times of medicine	Times of blank	Attractive rate (%)
A1	361	203	66.67
A2	130	70	85.71
A3	94	118	−20.34
A4	80	83	−3.61
A5	155	159	−2.52
A6	198	44	350.00
I1	273	184	48.37
I2	268	94	185.11
I3	279	260	7.31

3.4. *X-ray crystallography*

The crystal structure of compound **I2** was determined by X-ray single crystal diffraction. XRD data were collected on a Enraf-Nonius CAD-4 diffractometer equipped

Table 6. Attractive rates of dehydroabietic amides and imines to *Spodoptera litura*.

Compound	24 h	48 h	72 h
A1	206.79	38.14	66.67
A2	122.22	1.96	85.71
A3	−16.67	21.74	−20.34
A4	−80.00	−9.76	−3.61
A5	−36.67	−13.12	−2.52
A6	625.00	206.52	350.00
I1	−70.59	49.12	48.37
I2	300.00	206.78	185.11
I3	171.43	71.32	7.31

with Mo-Kα ($\lambda = 0.07103$ Å) at 293 K. A single crystal suitable for determination was mounted inside a glass fibre capillary. The structure of compound **I2** was solved by direct methods and refined by full-matrix least squares on F^2. All the hydrogen atoms were added in their calculated positions and all the non-hydrogen atoms were refined with anisotropic temperature factors. SHELXS97 were used to solve the structure and SHELTL were used to refine the structure (Sheldrick, 1997a and b).

3.5. *Insect attractant bioassay*

The *Pinus* diterpenic amides and imines were dissolved in acetone and tween 60 mixed solvent to form 0.01 g mL^{-1} solution. A 15 cm diameter leaf was dissolved in the test solution and another was dissolved in the same solvent for comparison; *S. litura* was introduced in a special equipment and the times of *S. litura* in different leaf plates was determined. The attractive rates were calculated using the following equation:

$$A = \frac{M - B}{B} \times 100\%,$$

in which A is attractive rate, M is the times of *S. litura* stopped in the medicine leaf plate and B is the times of *S. litura* stopped in the blank leaf plate.

4. Conclusions

Insect attractants are of great interest in pest management programmes; especially those from natural products are attracting great attention, as these kinds of products are environmentally friendly to animals and humans. *Pinus* dehydroabietic acids are widely distributed in the secretion of *Pinus* trees, and their special chemical structure and wide range of biological activities attracted our attention. Naturally occuring pine resin acids exhibited insect anti-feedant activities against some pests, and in our first thought, we wanted to obtain anti-feedants against *S. litura* from pine resin acids and their derivatives. However, to our surprise, the amides and imines from pine resin acids and those derivatives exhibited significant insect attractant activities to *S. litura*. From the bioassay results, fluorine-containing *Pinus* diterpenic amides and imines exhibited insect attractant

activities to *S. litura*; the fluorine introduced to the amides may result in the decrease of attractant rates of dehydroabietic amides (except **A6**), and the introduction of fluorine atom to the imines may result in the increase of attractive rates of dehydroabietic imines. The trifluoromethyl amide and *m*-fluoro imine exhibited higher activities; the attractive rates were four to seven times greater compared with blank. The characteristic group, the number, and the position of fluorine atoms in the benzene ring affect the insect attractant activity of compounds.

Acknowledgements

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (No. 30771690) and the Forestry Commonwealth Industry Special Foundation of China (No. 200704008).

References

Feio, S.S., Gigante, B., Roseiro, J.C., & Marcelo-Curto, M.J. (1999). Antimicrobial activity of diterpene resin acid derivatives. *Journal of Microbiological Methods, 35*, 201–206.

Feio, S.S., Roseiro, J.C., Gigante, B., & Marcelo-Curto, M.J. (1997). Method on multiwell plates for the evaluation of the antimicrobial activity of resin acid derivatives. *Journal of Microbiological Methods, 28*, 201–206.

Hao, N.C., Thi, N.C., Giang, H., Khoa, N.C., & Son, N.T. (1996). Synthesis and application of insect attractants in Vietnam. *Resources, Conservation and Recycling, 18*, 59–68.

Kushnir, S.R., Borisova, N.V., Radbil, A.B., Shmidt, E.N., Iosilevich, I.N., & Radbil, B.A. (2003). Synthesis of dehydroabietic chloride. *Russian Journal of Applied Chemistry, 76*(11), 1795–1797.

Momin, R.A., & Nair, M.G. (2002). Pest-managing efficacy of trans-asarone isolated from *Daucus carota* L. seeds. *Journal of Agricultural and Food Chemistry, 50*, 4475–4478.

San, F.A., Gordaliza, M., Salinero, M.A., & Miguel, J.M. (1993). Abietane acids: Sources, biological activities, and therapeutic uses. *Planta Medica, 59*, 485–489.

Sheldrick, G.M. (1997a). *SHELXL 97, Program for Crystal Structure Refinement*. Göttingen: University of Göttingen.

Sheldrick, G.M. (1997b). *SHELXS 97, Program for Crystal Structure Solution*. Göttingen: University of Göttingen.

Smith, E., Williamson, E., Zloh, M., & Gibbons, S. (2005). Isopimaric acid from *Pinus nigra* shows activity against multidrug -resistant and EMRSA strains of *Staphylococcus aureus*. *Phytotherapy Research, 19*, 538–542.

Ulusu, N.N., Ercil, D., Sakar, M.K., & Tezcan, E.F. (2002). Abietic acid inhibits lipoxygenase activity. *Phytotherapy Research, 16*, 88–90.

Wada, H., Kodato, S., Kawamori, M., Morikawa, T., Nakai, H., & Takeda, M. (1985). Antiulcer activity of dehydroabietic acid derivatives. *Chemical and Pharmaceutical Bulletin, 33*(9), 1472–1487.

Xua, X., Qianb, X., Lia, Z., Songa, G., & Chena, W. (2005). Synthesis and fungicidal activity of fluorine-containing phenylimino-thiazolidines derivatives. *Journal of Fluorine Chemistry, 126*, 297–300.

Yanez, B., Theoduloz, C., & Schmeda-Hirschmann, G. (2005). Gastroprotective and cytotoxic effect of dehydroabietic acid derivatives. *Pharmacological Research, 52*, 429–437.