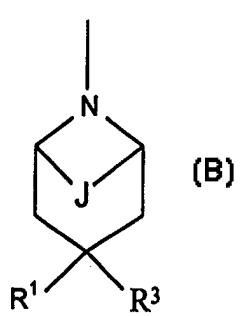




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07D 451/02, A01N 43/90</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/22462</b> <b>(43) International Publication Date:</b> 28 May 1998 (28.05.98)
<b>(21) International Application Number:</b> PCT/GB97/02987 <b>(22) International Filing Date:</b> 30 October 1997 (30.10.97) <b>(30) Priority Data:</b> 9623944.7 15 November 1996 (15.11.96) GB <b>(71) Applicant (for all designated States except US):</b> ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BISHOP, Nigel, Douglas [GB/GB]; (GB). URCH, Christopher, John [GB/GB]; (GB). LEWIS, Terence [GB/GB]; (GB). SUNLEY, Raymond, Leo [GB/GB]; (GB). SALMON, Roger [GB/GB]; (GB). GODFREY, Christopher, Richard, Ayles [GB/GB]; Zeneca Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire RG42 6ET (GB). <b>(74) Agents:</b> TIERNEY, Francis, John et al.; Zeneca Agrochemicals, Intellectual Property Dept., Jealott's Hill Research Station, P.O. Box 3538, Bracknell, Berkshire RG42 6YA (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> 8-AZABICYCLO[3.2.1]OCTANE-, 8-AZABICYCLO[3.2.1]OCT-6-ENE-, 9-AZABICYCLO[3.3.1]NONANE-, 9-AZA-3-OXABICYCLO[3.3.1]NONANE-, 9-AZA-3-THIABICYCLO[3.3.1]NONANE DERIVATIVES, THEIR PREPARATION AND THEIR USE AS INSECTICIDES		
<b>(57) Abstract</b>  <p>A compound of formula (I): P-R<sup>2</sup>-Q, where each of P and Q is, independently, a group of formula (B), wherein J is a bidentate group of formula -CH<sub>2</sub>-X-CH<sub>2</sub>- (wherein X is methylene, sulfur or oxygen), X'C=CY or X'WC-CYZ (wherein X', W, Y and Z are independently hydrogen, hydroxy, acyloxy, alkoxy, alkylsilyloxy or halogen); R<sup>1</sup> is an optionally substituted phenyl or 5- or 6-membered heterocyclic ring system containing from 1 to 3 heteroatoms individually selected from nitrogen, oxygen and sulfur atoms, and at least one unsaturation (double bond) between adjacent atoms in the ring, said heterocyclic ring being optionally fused to a benzene ring, wherein the substituents, if present, are selected from halogen atoms, cyano, alkyl, alkenyl, alkynyl, alkoxy, haloalkyl, haloalkenyl, alkylthio and alkyl amino groups, any of which groups contain up to six carbon atoms; R<sup>2</sup> is a bidentate linking group and is a substituted or unsubstituted alkylene, alkylenearyl, alkyleneheteroaryl, alkenylene, alkylenearylalkynylene, carbonyl or diacyl group, provided that when R<sup>2</sup> is alkenylene or alkylenearylalkynylene, said group does not have an unsaturated carbon atom bonding directly to the ring nitrogen of formula (B); R<sup>3</sup> is hydrogen, cyano, hydroxy, alkyl, alkoxy, amino, nitro, isocyanato, acylamino, hydroxyalkyl, optionally substituted heteroaryl, alkoxyalkyl, haloalkyl, haloalkoxyalkyl, aralkoxyalkyl, acyloxyalkyl, amidoximido, sulfonyloxyalkyl, aminoalkyl, alkoxyalkyl, alkoxyalkylamino, acylaminoalkyl, cyanoalkyl, imino, formyl, acyl or carboxylic acid or an ester or amide thereof, or alkenyl or alkynyl either of which is optionally substituted by halogen, alkoxy, cycloalkyl, optionally substituted aryl, optionally substituted heteroaryl or cyano; or an acid addition salt, quaternary ammonium salt or N-oxide derived therefrom; an insecticidal, acaricidal or nematocidal composition comprising a compound of formula (I) and a suitable carrier or diluent therefor; a method of combating and controlling insect, acarine or nematode pests at a locus which comprises treating the pests or the locus of the pests with an effective amount of a compound of formula (I) or a composition as hereinbefore described.</p> <div style="text-align: right;">  <p style="text-align: right;"><b>(B)</b></p> </div>		

**FOR THE PURPOSES OF INFORMATION ONLY**

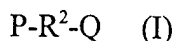
Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<b>AL</b>	Albania	<b>ES</b>	Spain	<b>LS</b>	Lesotho	<b>SI</b>	Slovenia
<b>AM</b>	Armenia	<b>FI</b>	Finland	<b>LT</b>	Lithuania	<b>SK</b>	Slovakia
<b>AT</b>	Austria	<b>FR</b>	France	<b>LU</b>	Luxembourg	<b>SN</b>	Senegal
<b>AU</b>	Australia	<b>GA</b>	Gabon	<b>LV</b>	Latvia	<b>SZ</b>	Swaziland
<b>AZ</b>	Azerbaijan	<b>GB</b>	United Kingdom	<b>MC</b>	Monaco	<b>TD</b>	Chad
<b>BA</b>	Bosnia and Herzegovina	<b>GE</b>	Georgia	<b>MD</b>	Republic of Moldova	<b>TG</b>	Togo
<b>BB</b>	Barbados	<b>GH</b>	Ghana	<b>MG</b>	Madagascar	<b>TJ</b>	Tajikistan
<b>BE</b>	Belgium	<b>GN</b>	Guinea	<b>MK</b>	The former Yugoslav Republic of Macedonia	<b>TM</b>	Turkmenistan
<b>BF</b>	Burkina Faso	<b>GR</b>	Greece			<b>TR</b>	Turkey
<b>BG</b>	Bulgaria	<b>HU</b>	Hungary	<b>ML</b>	Mali	<b>TT</b>	Trinidad and Tobago
<b>BJ</b>	Benin	<b>IE</b>	Ireland	<b>MN</b>	Mongolia	<b>UA</b>	Ukraine
<b>BR</b>	Brazil	<b>IL</b>	Israel	<b>MR</b>	Mauritania	<b>UG</b>	Uganda
<b>BY</b>	Belarus	<b>IS</b>	Iceland	<b>MW</b>	Malawi	<b>US</b>	United States of America
<b>CA</b>	Canada	<b>IT</b>	Italy	<b>MX</b>	Mexico	<b>UZ</b>	Uzbekistan
<b>CF</b>	Central African Republic	<b>JP</b>	Japan	<b>NE</b>	Niger	<b>VN</b>	Viet Nam
<b>CG</b>	Congo	<b>KE</b>	Kenya	<b>NL</b>	Netherlands	<b>YU</b>	Yugoslavia
<b>CH</b>	Switzerland	<b>KG</b>	Kyrgyzstan	<b>NO</b>	Norway	<b>ZW</b>	Zimbabwe
<b>CI</b>	Côte d'Ivoire	<b>KP</b>	Democratic People's Republic of Korea	<b>NZ</b>	New Zealand		
<b>CM</b>	Cameroon			<b>PL</b>	Poland		
<b>CN</b>	China	<b>KR</b>	Republic of Korea	<b>PT</b>	Portugal		
<b>CU</b>	Cuba	<b>KZ</b>	Kazakstan	<b>RO</b>	Romania		
<b>CZ</b>	Czech Republic	<b>LC</b>	Saint Lucia	<b>RU</b>	Russian Federation		
<b>DE</b>	Germany	<b>LI</b>	Liechtenstein	<b>SD</b>	Sudan		
<b>DK</b>	Denmark	<b>LK</b>	Sri Lanka	<b>SE</b>	Sweden		
<b>EE</b>	Estonia	<b>LR</b>	Liberia	<b>SG</b>	Singapore		

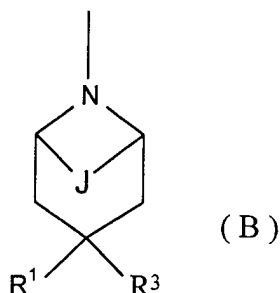
8-AZABICYCLO[3.2.1]OCTANE-, 8-AZABICYCLO[3.2.1]OCT-6-ENE-, 9-AZABICYCLO[3.3.1]NONANE-, 9-AZA-3-OXABICYCLO[3.3.1]NONANE-, 9-AZA-3-THIABICYCLO[3.3.1]NONANE DERIVATIVES, THEIR PREPARATION AND THEIR USE AS INSECTICIDES

This invention relates to novel bicyclic amine derivatives, to processes for preparing them, to insecticidal compositions comprising them and to methods of using them to combat and control insect pests.

5 A compound of formula (I):



where each of P and Q is, independently, a group of formula (B):



wherein J is a bidentate group of formula  $-CH_2-X-CH_2-$  (wherein X is methylene, sulfur or oxygen),  $X'C=CY$  or  $X'WC-CYZ$  (wherein X', W, Y and Z are independently hydrogen, hydroxy, acyloxy, alkoxy, alkylsilyloxy or halogen);  $R^1$  is an optionally substituted phenyl or 5- or 6-membered heterocyclic ring system containing from 1 to 3 heteroatoms individually selected from nitrogen, oxygen and sulfur atoms, and at least one unsaturation (double bond) between adjacent atoms in the ring, said heterocyclic ring being optionally fused to a benzene ring, wherein the substituents, if present, are selected from halogen atoms, cyano, alkyl, alkenyl, alkynyl, alkoxy, haloalkyl, haloalkenyl, alkylthio and alkyl amino groups, any of which groups contain up to six carbon atoms;  $R^2$  is a bidentate linking group and is a substituted or unsubstituted alkylene, alkylenearyl, alkyleneheteroaryl, alkenylene, alkylenearylalkylenyl, carbonyl or diacyl group, provided that when  $R^2$  is alkenylene or alkylenearylalkylenyl said group does not have an unsaturated carbon atom bonding directly to the ring nitrogen of formula (B);  $R^3$  is hydrogen, cyano, hydroxy, alkyl, alkoxy, amino, nitro, isocyanato, acylamino, hydroxyalkyl, optionally substituted heteroaryl, alkoxyalkyl, haloalkyl, halohydroxyalkyl, aralkyloxyalkyl, acyloxyalkyl, amidoximido, sulfonyloxyalkyl, aminoalkyl, alkoxycarbonylamino, acylaminoalkyl, cyanoalkyl, imino, formyl, acyl or carboxylic acid or an ester or amide thereof, or alkenyl or alkynyl either of which is optionally substituted by halogen, alkoxy, cycloalkyl, optionally substituted aryl, optionally

substituted heteroaryl or cyano; or an acid addition salt, quaternary ammonium salt or N-oxide derived therefrom.

It will be appreciated that the bicyclic amine compounds of formula (I) are capable of existing in more than one isomeric form since the groups  $R^1$  and  $R^3$  may be positioned in  
5 either an exo or endo relationship, and the present invention embraces within its scope both exo and endo forms and mixtures thereof in all proportions and also any further isomeric variants arising from cis and trans substitution patterns or chiral centres present in  $R^1$ ,  $R^2$  or  $R^3$ .

Examples of 5- and 6-membered heterocyclic ring systems represented by  $R^1$  include  
10 those based on pyridine, pyrazine, pyridazine, pirimidine, pyrrole, pyrazole, imidazole, 1,2,3- and 1,2,4-triazoles, furan, thiophene, oxazole, isoxazole, thiazole, isothiazole, 1,2,3- and 1,3,4-oxadiazoles, and 1,2,3- and 1,3,4-thiadiazoles, and partially reduced containing one double bond derived from these, as well as those based on oxathiole, dioxole, and dithiole rings containing one double bond. Preferably  $R^1$  represents a halo-substituted phenyl,  
15 pyridyl or diazinyl group.

When  $R^1$  is a 5- or 6- membered hererocyclic ring fused to a benzene ring it is preferably benzoxazole, indole, benzofuran, benzothiophen or benzimidazole.

Halogen includes fluorine, chlorine, bromine and iodine.

Alkyl moieties preferably contain from 1 to 6, more preferably from 1 to 4, carbon  
20 atoms. They can be in the form of straight or branched chains, for example methyl, ethyl, n- or iso-propyl, or n-, sec-, iso- or tert-butyl.

Haloalkyl is preferably  $C_{1-6}$  haloalkyl, especially fluoroalkyl (for example trifluoromethyl, 2,2,2-trifluoroethyl or 2,2-difluoroethyl) or chloroalkyl.

Alkenyl and alkynyl moieties preferably contain from 2 to 6, more preferably from 2  
25 to 4, carbon atoms. They can be in the form of straight or branched chains, and, where appropriate, the alkenyl moieties can be of either (E)- or (Z)-configuration. Examples are vinyl, allyl and propargyl.

Aryl includes naphthyl but is preferably phenyl.

Heteroaryl includes 5- and 6-membered aromatic rings containing one, two, three or  
30 four heteroatoms selected from the list comprising oxygen, sulphur and nitrogen and can be fused to benzenoid ring systems. Examples of heteroaryl are pyridinyl, pyrimidinyl,

pyridazinyl, pyrazinyl, triazinyl (1,2,3-, 1,2,4- and 1,3,5-), furyl, thienyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl (1,2,3- and 1,2,4-), tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, quinolinyl, isoquinolinyl, cinnolinyl, quinazolinyl, quinoxalinyl, indolinyl, isoindolinyl, benzofuranyl, benzothienyl and benzimidazolyl.

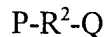
5           The alkylenedioxy group is a substituent for a ring and is especially C<sub>1-4</sub> alkylenedioxy. Alkylenedioxy groups are optionally substituted with halogen (especially fluorine) and are, for example, methylenedioxy (OCH<sub>2</sub>O) or difluoromethylenedioxy (OCF<sub>2</sub>O).

          Suitable acid addition salts include those with an inorganic acid such as hydrochloric,  
10   hydrobromic, sulfuric, nitric and phosphoric acids, or an organic carboxylic acid such as oxalic, tartaric, lactic, butyric, toluic, hexanoic and phthalic acids, or sulphonic acids such as methane, benzene and toluene sulphonic acids. Other examples of organic carboxylic acids include haloacids such as trifluoroacetic acid.

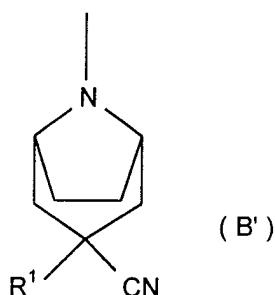
          In one particular aspect the present invention provides a compound of formula (I),  
15   wherein J is a bidentate group of formula -CH<sub>2</sub>-X-CH<sub>2</sub>- (wherein X is methylene, sulfur or oxygen), X'C=CY or X'WC-CYZ (wherein X', W, Y and Z are independently hydrogen, hydroxy, acyloxy (especially C<sub>1-4</sub> alkylcarbonyl), alkoxy (especially C<sub>1-4</sub> alkoxy), alkylsilyloxy (especially C<sub>1-4</sub> alkylsilyloxy) or halogen); R<sup>1</sup> is optionally substituted phenyl or optionally substituted 5- or 6-membered heterocyclic ring containing from 1 to 3 heteroatoms  
20   individually selected from nitrogen, oxygen and sulfur atoms, and at least one unsaturation (double bond) between adjacent atoms in the ring, said heterocyclic ring being optionally fused to a benzene ring, wherein the substituents, if present, are selected from halogen atoms, alkyl (especially C<sub>1-4</sub> alkyl), alkenyl (especially C<sub>2-4</sub> alkenyl), alkynyl (especially C<sub>2-4</sub> alkynyl), alkoxy (especially C<sub>1-4</sub> alkoxy), haloalkyl (especially C<sub>1-4</sub> haloalkyl), haloalkenyl  
25   (especially C<sub>2-4</sub> haloalkenyl), alkylthio (especially C<sub>1-4</sub> alkylthio), and alkyl amino (especially mono- or di- (C<sub>1-4</sub> alkyl)amino, such as mono- or di- (C<sub>1-3</sub> alkyl)amino) groups; R<sup>2</sup> is a bidentate linking group and is a substituted or unsubstituted alkylene (such as C<sub>1-8</sub> alkylene optionally substituted with halogen, C<sub>1-4</sub> alkyl or hydroxy), alkylenearyl (such as C<sub>1-6</sub> alkylenephenyl optionally substituted with halogen, C<sub>1-4</sub> alkyl or hydroxy),  
30   alkyleneheteroaryl (such as C<sub>1-6</sub> alkyleneheteroaryl optionally substituted with halogen, C<sub>1-4</sub> alkyl or hydroxy; wherein the heteroaryl is especially pyridinyl, pyrimidinyl or 1,2,4-

thiazolyl), alkenylene (especially C<sub>4-6</sub> alkenylene optionally substituted with halogen or C<sub>1-4</sub> alkyl), alkylenylarylalkylenyl (especially C<sub>3-6</sub> alkenylenylphenyl(C<sub>3-6</sub>)alkenylenyl optionally substituted with halogen or C<sub>1-4</sub> alkyl), carbonyl or diacyl (such as C(O)R<sup>4</sup>C(O) wherein R<sup>4</sup> is (CH<sub>2</sub>)<sub>n</sub> or a phenyl ring (optionally substituted with halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> haloalkyl, C<sub>1-4</sub> alkoxy or C<sub>1-4</sub> haloalkoxy) and n is 0 or an integer from 1-6) group, provided that when R<sup>2</sup> is alkenylene or alkylenylarylalkylenyl said group does not have an unsaturated carbon atom bonding directly to the ring nitrogen of formula (B), and when said groups are substituted with halogen or hydroxy said substituents are not on the carbon bonding directly to the ring nitrogen of formula (B); R<sup>3</sup> is cyano, hydroxy, alkyl (especially C<sub>1-4</sub> alkyl), alkoxy (especially C<sub>1-4</sub> alkoxy), amino (especially unsubstituted, mono- or di-(C<sub>1-4</sub>)alkylamino or amino substituted with a formyl group), nitro, isocyanato, acylamino (especially C<sub>1-4</sub> alkylcarbonylamino or phenylcarbonylamino), hydroxyalkyl (especially monohydroxy(C<sub>1-4</sub>)alkyl), optionally substituted heteroaryl (especially tetrazole, oxadiazole, pyridinyl or pyrimidinyl optionally substituted by halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> haloalkyl, C<sub>1-4</sub> alkoxy or C<sub>1-4</sub> haloalkoxy), alkoxyalkyl (especially C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl), haloalkyl (especially C<sub>1-4</sub> haloalkyl), halohydroxyalkyl (especially C<sub>1-4</sub> halohydroxyalkyl, such as 2-hydroxy-1,1-difluoroethyl), aralkyloxyalkyl (especially phenyl(C<sub>1-4</sub>)alkoxy(C<sub>1-4</sub>)alkyl), acyloxyalkyl (especially C<sub>1-4</sub> alkylcarbonyloxy(C<sub>1-4</sub>)alkyl), amidoximido (C(NH<sub>2</sub>)NOH), sulfonyloxyalkyl (especially sulfonyloxy(C<sub>1-4</sub>)alkyl), aminoalkyl (especially amino(C<sub>1-4</sub>)alkyl), alkoxy carbonylamino (especially C<sub>1-4</sub> alkoxy carbonylamino), acylaminoalkyl (especially C<sub>1-4</sub> alkylcarbonylamino(C<sub>1-4</sub>)alkyl or phenylcarbonylamino(C<sub>1-4</sub>)alkyl), cyanoalkyl (especially C<sub>1-4</sub> cyanoalkyl), imino (especially hydroxyimino (HON=CH) or C<sub>1-4</sub> alkoxyimino), formyl, acyl (especially C<sub>1-4</sub> alkylcarbonyl) or carboxylic acid or an ester (especially a C<sub>1-4</sub> alkyl ester) or amide (especially an unsubstituted or an N,N-di(C<sub>1-4</sub>)alkyl amide) thereof, or alkenyl (especially C<sub>2-4</sub> alkenyl) or alkynyl (especially C<sub>2-4</sub> alkynyl) either of which is optionally substituted by halogen, alkoxy (especially C<sub>1-4</sub> alkoxy), cycloalkyl (especially C<sub>3-7</sub> cycloalkyl, such as cyclopropyl or cyclohexyl), optionally substituted aryl (especially phenyl optionally substituted by halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> haloalkyl, C<sub>1-4</sub> alkoxy or C<sub>1-4</sub> haloalkoxy), optionally substituted heteroaryl (especially pyridinyl or pyrimidinyl optionally substituted by halogen, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> haloalkyl, C<sub>1-4</sub> alkoxy or C<sub>1-4</sub> haloalkoxy) or cyano; or an acid addition salt, quaternary ammonium salt or N-oxide derived therefrom.

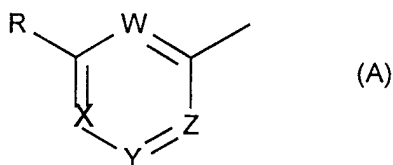
In one particular aspect the present invention provides compounds having the general formula (I):



where each of P and Q is a group of formula (B'):



wherein R<sup>1</sup> represents a group of formula (A):



where each of W, X, Y and Z represents either a group CR or the nitrogen atom, provided that not more than two of W, X, Y and Z represent the nitrogen atom and where each R present is independently selected from hydrogen and halogen atoms and cyano, amino, hydrazino, acylamino, hydroxy, alkyl, hydroxyalkyl, alkoxy, haloalkyl, haloalkoxy, alkenyl, alkenyloxy, alkoxyalkenyl, alkynyl, carboxylic acyl, alkoxycarbonyl, aryl and heterocyclyl groups, said groups comprising up to 6 carbon atoms, and wherein R<sup>2</sup> represents a bidentate linking group selected from substituted and unsubstituted alkylene, alkenylene, alkylenylarylalkylenyl, carbonyl, and diacyl groups; and acid addition salts and quaternary ammonium salts and N-oxides derived therefrom. R<sup>1</sup> is preferably a halo-substituted phenyl, pyridyl or diazinyl group.

In yet another aspect the present invention provides a compound of formula (I) wherein J is -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-, CH=CH or CH<sub>2</sub>-CH<sub>2</sub>.

In another aspect the present invention provides a compound of formula (I), wherein Ar is phenyl, pyridinyl, pyridazinyl or pyrazinyl, all being optionally substituted with halogen (especially fluorine, chlorine or bromine), C<sub>1-4</sub> alkyl (especially methyl), C<sub>1-4</sub> alkoxy (especially methoxy), C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl or cyano.

In a further aspect the present invention provides a compound of formula (I) wherein  $R^1$  is an optionally halogen (especially chlorine or fluorine),  $C_{1-4}$  alkoxy (especially methoxy or ethoxy) or cyano substituted phenyl group or an optionally halogen (especially chlorine or fluorine),  $C_{1-4}$  alkoxy (especially methoxy or ethoxy) or cyano substituted pyridyl,  
 5 pyridazinyl or pyrazinyl group (especially a chlorine or bromine substituted pyridinyl group).

In a preferred aspect the present invention provides compounds of formula (I) where  $R^1$  represents an optionally halogen substituted phenyl group or an optionally halogen substituted pyridyl, pyridazinyl or pyrazinyl group and  $R^2$  represents alkylene of up to six carbon atoms or a dicarboxylic acyl group; and acid addition salts thereof.

10 In a further aspect the present invention provides a compound of formula (I) wherein  $R^1$  is an optionally halogen (especially chlorine or bromine) substituted pyridyl group.

In a still further aspect the present invention provides a compound of formula (I) wherein  $R^2$  is alkylene containing up to 8 carbon atoms.

One particularly preferred group of compounds are those wherein  $R^1$  represents an  
 15 optionally halogen substituted phenyl or pyridyl group and  $R^2$  represents alkylene containing up to 4 carbon atoms, or oxalyl.

An especially preferred group of compounds are those wherein  $R^1$  represents a 5-halopyrid-3-yl group and  $R^2$  represents the dimethylene group.

It is preferred that  $R^3$  is cyano.

20 It is preferred that J is  $CH_2-CH_2$  or  $CH=CH$ .

Specific compounds of formula (I) according to the invention include those set out in Table I below in which  $R^3$  is cyano, J is  $CH_2-CH_2$ , the groups P and Q are the same and the groups represented by  $R^1$  and  $R^2$  are given for each compound, together with the melting point ( $^{\circ}C$ ).

25

TABLE I

Compound No	$R^1$	$R^2$	Melting Point
1	5-chloropyrid-3-yl	oxalyl	105-108 $^{\circ}C$
2	5-chloropyrid-3-yl	dimethylene	166-170 $^{\circ}C$ (dec.)
3	2,3-difluorophenyl	dimethylene	
4	pentafluorophenyl	tetramethylene	



Compound No	R <sup>1</sup>	R <sup>2</sup>	Melting Point
5	2,3-dichlorophenyl	dimethylene	
6	3,5-difluorophenyl	dimethylene	
7	3,5-difluorophenyl	oxalyl	
8	5-chloropyrid-3-yl	hexamethylene	
9	5-chloropyrid-3-yl	1,4-xyxylenyl	
10	5-chloropyrid-3-yl	1,4-benzenedicarbonyl	
11	5-chloropyrid-3-yl	malonyl	
12	5-chloropyrid-3-yl	succinyl	253-255°C
13	5-chloropyrid-3-yl	carbonyl	186-188°C (dec.)
14	pyrid-3-yl	dimethylene	
15	6-chloropyridazin-3-yl	dimethylene	
16	6-chloropyrid-3-yl	dimethylene	
17	6-chloropyrazin-2-yl	dimethylene	
18	2,6-dichloropyrimid-4-yl	dimethylene	
19	5-bromopyrid-3-yl	oxalyl	
20	5-ethoxypyrid-3-yl	dimethylene	
21	5-bromopyrid-3-yl	dimethylene	
22	5-chloropyrid-3-yl	methylene	
23	5-chloropyrid-3-yl	3-methylene-1,2,4-thiadiazol-5-yl	oil

The preparation of the compounds of formula (I) may be accomplished by adaptation of methods described in the literature, by use of one or more of the following synthetic techniques described below and further illustrated in the Examples, or by combining

5 literature methods with those methods described below. The group R<sup>4</sup> in formulae (III)-(VII) is an alkyl or phenylalkyl (especially benzyl) group.

The compounds of formula (I) in which the tropane nitrogen atoms are linked as amines can be prepared by reacting compounds of formula (II) with a compound of formula

LR<sup>2</sup>L, where L is a suitable leaving group (such as halide or triflate), in the presence of a suitable base, such as potassium carbonate.

Alternatively, compounds of formula (I) in which the tropane nitrogen atoms are linked as amines can be prepared from compounds of formula (II) by reductive amination with a dialdehyde (OHC-R<sup>5</sup>-CHO; where R<sup>2</sup> is H<sub>2</sub>C-R<sup>5</sup>-CH<sub>2</sub>) in the presence of a suitable reducing agent such as formic acid.

Compounds of formula (I) in which the tropane nitrogen atoms are linked as amides can be prepared by treating compounds of formula (II) with a suitable base, such as sodium hydroxide, in the presence of a diacid chloride ClOC-R<sup>5</sup>-COCl, where R<sup>2</sup> is

OC-R<sup>5</sup>-CO). Compounds of formula P-R<sup>2</sup>-Q which are oxamides are prepared from the corresponding compound of formula (II) in a similar way using oxalyl chloride.

Compounds of formula (I) wherein R<sup>3</sup> is other than cyano can be made by adapting methods described in the for either the conversion of a cyano group to the desired R<sup>3</sup> group or the replacement of a cyano group with the desired R<sup>3</sup> group.

Compounds of formula (II) (which are compounds of formula (I) wherein R is hydrogen) can be prepared by deprotecting compounds of formula (III) by, for instance, either: (i) treating them with a chloroformate ester (such as vinyl chloroformate) and subjecting the carbamate so formed to acid hydrolysis (with for example, hydrochloric acid); or (ii) treating them with an azodicarboxylate (such as diethyl azodicarboxylate) at a suitably elevated temperature.

Compounds of formula (III) wherein R<sup>3</sup> is cyano can be prepared by treating compounds of formula (IV) first with a suitable base, such as lithium diisopropylamide (LDA) or lithium bis(trimethylsilyl)amide, and then reacting the product so formed with a compound R<sup>1</sup>Hal, wherein Hal is a halogen.

Compounds of formula (IV), wherein R<sup>3</sup> is cyano, can be prepared by treating compounds of formula (V) with tosylmethyl isocyanide (also known as (4-tolylsulfonyl)methylisocyanide in the presence of a suitable base, such as potassium ethoxide or potassium tert-butoxide.

Alternatively compounds of formula (IV), wherein R<sup>3</sup> is cyano, can be prepared from compounds of formula (VI) by treatment with thionyl chloride to give compounds of formula (VII) followed by treatment with cyanide as described in J. Am. Chem. Soc., 1958, **80**, 4677.

Compounds of formula (V) can be prepared by methods analogous to the Robinson tropinone synthesis. (See, for example, J. Chem. Soc., 1917, 111, 762, and Organic Synthesis (Collective Volume 4), p 816.)

Compounds of formula (V) wherein J is  $\text{CH}_2\text{CH}_2$  can be prepared by reacting an amine of formula  $\text{R}^4\text{NH}_2$  with cyclohepta-2,6-dienone (VIII). (See, for example, Tetrahedron, 1973, 155, Bull. Chem. Soc. Jpn., 1971, 44, 1708 and J. Org. Chem., 1971, 36, 1718.)

3-Cyano-9-azabicyclo[3.3.1]nonane can be prepared by demethylating 3-cyano-9-methyl-9-azabicyclo[3.3.1]nonane by, for instance, treatment it with a chloroformate ester (such as vinyl chloroformate) and subjecting the carbamate so formed to acid hydrolysis.

Compounds of formulae (I) or (II) wherein J is  $\text{CH}=\text{CH}$  can be prepared by heating a corresponding compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CHZ}$  (wherein Z is a suitable group, such as a thiono-4-tolyloxy group) in a suitable solvent (such as xylene) at a suitable temperature (such as reflux).

Compounds of formulae (I) or (II) wherein J is  $\text{CH}_2\text{CHZ}$  (wherein Z is a suitable group, such as a thiono-4-tolyloxy group) can be prepared by treating corresponding compounds of formula (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OH})$  with a suitable chloroformate (such as 4-tolyl chlorothionoformate) in the presence of a suitable base (such as N,N-dimethylaminopyridine).

Compounds of formulae (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OH})$  can be prepared by acid hydrolysis of corresponding compounds of formula (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OZ}')$  wherein Z' is a hydrolysable group (such as tert-butyldimethylsilyl).

A compound of formula (II) wherein J is  $\text{CH}_2\text{CH}(\text{OZ}')$  wherein Z' is hydrogen or a hydrolysable group (such as tert-butyldimethylsilyl) and  $\text{R}^3$  is cyano can be prepared by reacting a corresponding compound of formula (IV) with a suitable base, such as lithium diisopropylamide (LDA) or lithium bis(trimethylsilyl)amide, and reacting the product so formed with a compound  $\text{R}^1\text{Hal}$ , wherein Hal is a halogen.

A compound of formula (IV) wherein J is  $\text{CH}_2\text{CH}(\text{OZ}')$  wherein Z' is hydrogen or a hydrolysable group (such as tert-butyldimethylsilyl) and  $\text{R}^3$  is cyano can be prepared by treating a corresponding compound of formula (V) with tosylmethyl isocyanide (also known

as (4-tolylsulfonyl)methylisocyanide in the presence of a suitable base, such as potassium tert-butoxide.

A compound of formula (V) wherein J is  $\text{CH}_2\text{CH}(\text{OZ}')$  wherein  $\text{Z}'$  is a hydrolysable group (such as tert-butyldimethylsilyl) and  $\text{R}^3$  is cyano can be prepared by reacting a  
5 compound of formula (V) wherein J is  $\text{CH}_2\text{CH}(\text{OH})$  and  $\text{R}^3$  is cyano with a compound  $\text{Z}'\text{L}$  wherein L is a leaving group.

Alternatively a compound of formula (I) wherein J is  $\text{CH}=\text{CH}$  can be prepared by dehydrating a compound of formula (I) wherein J is  $\text{CH}_2\text{CH}(\text{OH})$  with a suitable dehydrating agent, such as diethylaminosulfurtrifluoride.

10 A compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CHF}$  can be prepared by fluorinating a corresponding compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OH})$  with, for example, a mixture of hydrogen fluoride and sulfur trifluoride.

A compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{C}(=\text{O})$  can be prepared by reacting a corresponding compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OH})$  with a  
15 suitable acid chloride (such as oxalyl chloride) at a suitable temperature (such as below -  $50^\circ\text{C}$ ).

A compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CF}_2$  can be prepared by fluorinating a corresponding compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{C}(=\text{O})$  with, for example, diethylamino-sulfurtrifluoride.

20 A compound of formula (I) or (II) wherein J is  $\text{CH}=\text{CH}$  can be prepared by reacting a corresponding compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OZ}')$ , wherein  $\text{Z}'$  is a suitable group (such as  $\text{SO}_2\text{CH}_3$ ) with a suitable amine (such as 1,8-diazabicyclo[5.4.0]undec-7-ene).

A compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OZ}')$ , wherein  $\text{Z}'$  is a suitable  
25 group (such as  $\text{SO}_2\text{CH}_3$ ) can be prepared by reacting a corresponding compound of formula (I) or (II) wherein J is  $\text{CH}_2\text{CH}(\text{OH})$  with a suitable acid chloride (such as mesyl chloride).

In further aspects the present invention provides processes for preparing compounds of formula (I), as hereinbefore described.

In a still further aspect the invention provides a method of combating insect and like  
30 pests at a locus by applying to the locus or the pests an insecticidally effective amount of an

insecticidal composition comprising a compound of formula (I) or an acid addition salt, quaternary ammonium salt or N-oxide derived therefrom.

The compounds of formula (I) can be used to combat and control infestations of insect pests such as Lepidoptera, Diptera, Homoptera and Coleoptera (including Diabrotica i.e. corn rootworms) and also other invertebrate pests, for example, acarine pests. The insect and acarine pests which may be combated and controlled by the use of the invention compounds include those pests associated with agriculture (which term includes the growing of crops for food and fibre products), horticulture and animal husbandry, forestry, the storage of products of vegetable origin, such as fruit, grain and timber, and also those pests associated with the transmission of diseases of man and animals. Examples of insect and acarine pest species which may be controlled by the compounds of formula (I) include: Myzus persicae (aphid), Aphis gossypii (aphid), Aphis fabae (aphid), Aedes aegypti (mosquito), Anopheles spp. (mosquitos), Culex spp. (mosquitos), Dysdercus fasciatus (capsid), Musca domestica (housefly), Pieris brassicae (white butterfly), Plutella xylostella (diamond back moth), Phaedon cochleariae (mustard beetle), Aonidiella spp. (scale insects), Trialeurodes spp. (white flies), Bemisia tabaci (white fly), Blattella germanica (cockroach), Periplaneta americana (cockroach), Blatta orientalis (cockroach) Spodoptera littoralis (cotton leafworm), Heliothis virescens (tobacco budworm) Chortiocetes terminifera (locust), Diabrotica spp. (rootworms), Agrotis spp. (cutworms), Chilo partellus (maize stem borer), Nilaparvata lugens (planthopper), Nephotettix cincticeps (leafhopper), Panonychus ulmi (European red mite), Panonychus citri (citrus red mite), Tetranychus urticae (two-spotted spider mite), Tetranychus cinnabarinus (carmine spider mite), Phyllcoptruta oleivora (citrus rust mite), Polyphagotarsonemus latus (broad mite) and Brevipalpus spp. (mites). Further examples include insects which adversely affect the health of the public or of animals.

In order to apply the compounds of formula (I) to the locus of the nematode, insect or acarid pest, or to a plant susceptible to attack by the nematode, insect or acarid pest, the compound is usually formulated into a composition which includes in addition to a compound of formula (I) a suitable inert diluent or carrier material, and, optionally, a surface active agent. The amount of composition generally applied for the control of nematode pests gives a rate of active ingredient from 0.01 to 10 kg per hectare, preferably from 0.1 to 6 kg per hectare.

Thus in another aspect the present invention provides a insecticidal, acaricidal or nematocidal composition comprising an insecticidally, acaricidally or nematocidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor.

The compositions can be applied to the soil, plant or seed, to the locus of the pests, or  
5 to the habitat of the pests, in the form of dusting powders, wettable powders, granules (slow or fast release), emulsion or suspension concentrates, liquid solutions, emulsions, seed dressings, fogging/smoke formulations or controlled release compositions, such as microencapsulated granules or suspensions.

Dusting powders are formulated by mixing the active ingredient with one or more  
10 finely divided solid carriers and/or diluents, for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers.

Granules are formed either by absorbing the active ingredient in a porous granular  
15 material for example pumice, attapulgite clays, Fuller's earth, kieselguhr, diatomaceous earths, ground corn cobs, and the like, or on to hard core materials such as sands, silicates, mineral carbonates, sulphates, phosphates, or the like. Agents which are commonly used to aid in impregnation, binding or coating the solid carriers include aliphatic and aromatic petroleum solvents, alcohols, polyvinyl acetates, polyvinyl alcohols, ethers, ketones, esters,  
20 dextrans, sugars and vegetable oils. with the active ingredient. Other additives may also be included, such as emulsifying agents, wetting agents or dispersing agents.

Microencapsulated formulations (microcapsule suspensions CS) or other controlled release formulations may also be used, particularly for slow release over a period of time, and for seed treatment.

25 Alternatively the compositions may be in the form of liquid preparations to be used as dips, irrigation additives or sprays, which are generally aqueous dispersions or emulsions of the active ingredient in the presence of one or more known wetting agents, dispersing agents or emulsifying agents (surface active agents). The compositions which are to be used in the form of aqueous dispersions or emulsions are generally supplied in the form of an  
30 emulsifiable concentrate (EC) or a suspension concentrate (SC) containing a high proportion of the active ingredient or ingredients. An EC is a homogeneous liquid composition, usually

containing the active ingredient dissolved in a substantially non-volatile organic solvent. An SC is a fine particle size dispersion of solid active ingredient in water. In use, the concentrates are diluted in water and applied by means of a spray to the area to be treated.

Suitable liquid solvents for ECs include methyl ketones, methyl isobutyl ketone, 5 cyclohexanone, xylenes, toluene, chlorobenzene, paraffins, kerosene, white oil, alcohols, (for example, butanol), methylnaphthalene, trimethylbenzene, trichloroethylene, N-methyl-2-pyrrolidone and tetrahydrofurfuryl alcohol (THFA).

Wetting agents, dispersing agents and emulsifying agents may be of the cationic, anionic or non-ionic type. Suitable agents of the cationic type include, for example, 10 quaternary ammonium compounds, for example cetyltrimethyl ammonium bromide. Suitable agents of the anionic type include, for example, soaps, salts of aliphatic monoesters of sulphuric acid, for example sodium lauryl sulphate, salts of sulphonated aromatic compounds, for example sodium dodecylbenzenesulphonate, sodium, calcium or ammonium lignosulphonate, or butylnaphthalene sulphonate, and a mixture of the sodium salts of 15 diisopropyl- and triisopropylnaphthalene sulphonates. Suitable agents of the non-ionic type include, for example, the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol or cetyl alcohol, or with alkyl phenols such as octyl phenol, nonyl phenol and octyl cresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene 20 oxide, and the lecithins.

These concentrates are often required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates may contain 10-85% by weight of the active ingredient or 25 ingredients. When diluted to form aqueous preparations such preparations may contain varying amounts of the active ingredient depending upon the purpose for which they are to be used.

The compounds of formula (I) may also be formulated as powders (dry seed treatment DS or water dispersible powder WS) or liquids (flowable concentrate FS, liquid 30 seed treatment LS, or microcapsule suspension CS) for use in seed treatments.

In use the compositions are applied to the insect pests, to the locus of the pests, to the habitat of the pests, or to growing plants liable to infestation by the pests, by any of the known means of applying pesticidal compositions, for example, by dusting, spraying, or incorporation of granules.

- 5       The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as insecticides, synergists, herbicides, fungicides or plant growth regulators where appropriate. Suitable additional active ingredients for inclusion in admixture with a compound of formula (I) may be compounds which will broaden the spectrum of activity of the compositions of the
- 10       invention or increase their persistence in the location of the pest. They may synergise the activity of the compound of formula (I) or complement the activity for example by increasing the speed of effect or overcoming repellency. Additionally multi-component mixtures of this type may help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient included will depend upon the
- 15       intended utility of the mixture and the type of complementary action required. Examples of suitable insecticides include the following:
- a)       Pyrethroids such as permethrin, esfenvalerate, deltamethrin, cyhalothrin in particular lambda-cyhalothrin, biphenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids for example ethofenprox, natural pyrethrin, tetramethrin, s-bioallethrin, fenfluthrin,
- 20       prallethrin and 5-benzyl-3-furylmethyl-(E)-(1R,3S)-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl) cyclopropane carboxylate;
- b)       Organophosphates such as profenofos, sulprofos, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, profenophos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chloropyrifos,
- 25       phosalone, terbufos, fensulfothion, fonofos, phorate, phoxim, pyrimiphos-methyl, pyrimiphos-ethyl, fenitrothion or diazinon;
- c)       Carbamates (including aryl carbamates) such as pirimicarb, cloethocarb, carbofuran, furathiocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur or oxamyl;
- 30       d) Benzoyl ureas such as triflumuron, or chlorfluazuron;
- e) Organic tin compounds such as cyhexatin, fenbutatin oxide, azocyclotin;



- f) Macrolides such as avermectins or milbemycins, for example such as abamectin, ivermectin, and milbemycin;
- g) Hormones and pheromones;
- h) Organochlorine compounds such as benzene hexachloride, DDT, chlordane or dieldrin;
- 5 i) Amidines, such as chlordimeform or amitraz;
- j) Fumigant agents;
- k) Imidacloprid;
- l) spinosad.

In addition to the major chemical classes of insecticide listed above, other  
10 insecticides having particular targets may be employed in the mixture if appropriate for the intended utility of the mixture. For instance selective insecticides for particular crops, for example stemborer specific insecticides for use in rice such as cartap or buprofezin can be employed. Alternatively insecticides specific for particular insect species/stages for example  
15 ovo-larvicides such as chlofentezine, flubenzimine, hexythiazox and tetradifon, motilicides such as dicofol or propargite, acaricides such as bromopropylate, chlorobenzilate, or growth regulators such as hydramethylnon, cyromazine, methoprene, chlorofluazuron and diflubenzuron may also be included in the compositions.

Examples of suitable synergists for use in the compositions include piperonyl butoxide, sesamax, safroxan and dodecyl imidazole.

20 Suitable herbicides, fungicides and plant-growth regulators for inclusion in the compositions will depend upon the intended target and the effect required.

An example of a rice selective herbicide which can be included is propanil, an example of a plant growth regulator for use in cotton is "Pix", and examples of fungicides for use in rice include blasticides such as blasticidin-S. The ratio of the compound of formula (I)  
25 to the other active ingredient in the composition will depend upon a number of factors including type of target, effect required from the mixture etc. However in general, the additional active ingredient of the composition will be applied at about the rate at which it is usually employed, or at a slightly lower rate if synergism occurs.

The invention is illustrated by the following Examples. Examples 1-5 illustrate the  
30 preparation of a range of compounds of formula (I). Examples 6-13 illustrate compositions suitable for the application of the compounds of formula (I) according to the invention. The

following ingredients are referred to by their Registered Trade Marks and have the composition as shown below.

<u>Registered Trade Mark</u>	<u>Composition</u>
Synperonic NP8 } Synperonic NP13 } Synperonic OP10 }	Nonylphenol-ethylene oxide condensate
Aromasol H	Alkylbenzene solvent
Solvesso 200	Inert organic diluent
Keltrol	Polysaccharide

The starting material used in Examples 1 and 2 below was prepared from tropinone  
5 by the following procedure.

Potassium tert-butoxide (22.4g) was added portionwise to a stirred mixture of tropinone (11.58g) and tosylmethyl isocyanide (21.2g) in dimethoxyethane (240ml) and ethanol (8ml) at 0°C under nitrogen at such a rate to maintain the temperature between 0°C and 10°C. The mixture was then allowed to warm to room temperature and stirred for a further 4 hours. After  
10 standing at room temperature for 3 days the mixture was filtered and the solid residue washed with dimethoxyethane. The filtrate was evaporated under reduced pressure and chromatographed [SiO<sub>2</sub>; dichloromethane:methanol (90:10)] to give exo-3-cyano-8-methyl-8-azabicyclo[3.2.1]octane (9.1g).

exo-3-Cyano-8-methyl-8-azabicyclo[3.2.1]octane (0.5g) in tetrahydrofuran (3ml) was  
15 added to a solution of lithium diisopropylamide [made by adding n-butyl lithium (1.6ml of a 2.5M solution in hexane) to diisopropylamine (0.4g) in tetrahydrofuran (3ml)] at -25°C under nitrogen. After a further 15 minutes at -25°C 3,5-dichloropyridine (0.588g) in tetrahydrofuran (3ml) was added at -78°C. After 1 hour at the mixture was allowed to warm to room temperature and stand overnight. Water was then added and the resulting mixture  
20 extracted with ethyl acetate (x3). The combined extracts were washed with brine and water, dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. Chromatography [SiO<sub>2</sub>; dichloromethane:methanol (90:10)] gave exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-methyl-8-azabicyclo[3.2.1]octane (0.249g).

Vinyl chloroformate (2.6ml) in tetrahydrofuran (5ml) was added to a stirred solution of exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-methyl-8-azabicyclo[3.2.1]octane (2.6g) in tetrahydrofuran (25ml) at 0°C. The mixture was allowed to warm to room temperature over 1 hour, refluxed for 2 hours and then allowed to cool to room temperature. After 20 hours the mixture was partitioned between water and ethyl acetate and the organic layer was separated, washed with water and dried (MgSO<sub>4</sub>). Evaporation under reduced pressure gave exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-(vinylloxycarbonyl)-8-azabicyclo[3.2.1]octane (2.0g).

exo-3-(5-Chloropyrid-3-yl)-endo-3-cyano-8-(vinylloxycarbonyl)-8-azabicyclo[3.2.1]octane (2.6g) was dissolved in methanol (50ml) and concentrated hydrochloric acid (7ml) added. The mixture was refluxed for 3 hours after which the mixture was evaporated under reduced pressure and basified with aqueous sodium carbonate. The resulting mixture was extracted with ethyl acetate and evaporated under reduced pressure to give a brown solid. This was then washed with hexane to give exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane (1.2g).

#### EXAMPLE 1

This Example illustrates the preparation of 8,8'-oxalyldi(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane) (Compound No. 1 Table I).

Triethylamine (0.28ml) followed by oxalyl chloride (0.088ml) were added to a stirred solution of exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane (0.50g) in dichloromethane (10ml) at room temperature. After 2 hours dichloromethane was added and the mixture washed with water (x2) and brine, dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. Chromatography [SiO<sub>2</sub>; ethyl acetate:hexane (10:90)] followed by chromatography [SiO<sub>2</sub>; dichloromethane:methanol (95:4)] gave 8,8'-oxalyldi(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane) (0.45g) m.p. 105-108°C.

#### EXAMPLE 2

This Example illustrates the preparation of 1,2-di-8,8'-(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane)ethane (Compound No. 2 Table I).

exo-3-(5-Chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane (0.50g), 1,2-dibromoethane (1.0ml) and potassium carbonate (0.552g) were refluxed in ethanol (5ml) for

3 hours and then left to stand overnight. 1,2-Dibromoethane (2.0ml) was then added and the mixture heated under reflux for 7 hours. The mixture was then filtered (celite) and the residue washed through with dichloromethane. The combined organic fractions were evaporated under reduced pressure and chromatographed [ $\text{SiO}_2$ ; dichloromethane:methanol (95:5)] to give 1,2-di-8,8'-(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane)ethane (0.315g) m.p. 166-170°C (decomposed).

### EXAMPLE 3

This Example illustrates the preparation of 8,8'-carbonyldi(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane) (Compound No. 13 Table I).

10 Triethylamine (0.30ml) was added to a stirred solution of exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane (0.50g) in dichloromethane (10ml) at room temperature. Phosgene (0.52ml of a 1.93M solution in toluene) was then added and the mixture allowed to stand over the weekend. The mixture was then diluted with dichloromethane, washed with water (x2) and brine, dried ( $\text{MgSO}_4$ ) and evaporated under reduced pressure. Chromatography [ $\text{SiO}_2$ ; diethyl ether] gave of 8,8'-carbonyldi(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane (0.312g) m.p. 186-188°C (dec.).

### EXAMPLE 4

This Example illustrates the preparation of 8,8'-succinyldi(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane) (Compound No. 12 Table I).

20 Succinyl chloride (0.25ml) was added to a stirred mixture of exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane (1.168g) in dichloromethane (10ml) and 1M potassium carbonate (10ml). After 5 hours the mixture was allowed to stand overnight and then partitioned between saturated sodium bicarbonate and dichloromethane. The organic layer was separated, dried and evaporated under reduced pressure. Ethyl acetate was added to the residue and the mixture filtered to give a solid product which was recrystallised from methanol/ethyl acetate to give 8,8'-succinyldi(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane) (0.476g) m.p. 253-255°C.

### EXAMPLE 5

This Example illustrates the preparation of exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-((5-(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]oct-8-yl)-1,2,4-thiadiazol-3-yl)methyl)-8-azabicyclo[3.2.1]octane (Compound No. 23 Table I).

exo-3-(5-Chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]octane (0.248g), 3-chloromethyl-5-chloro-1,2,4-thiadiazole (0.186g), potassium carbonate (0.345g) and potassium iodide (0.02g) were refluxed in ethanol (2ml) for 1.5 hours. The mixture was then cooled to room temperature, water was added and the mixture extracted with  
 5 dichloromethane (x2). The combined extracts were washed with brine, dried (MgSO<sub>4</sub>) and evaporated under reduced pressure. Chromatography [SiO<sub>2</sub>; dichloromethane:methanol (98:2)] gave exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-((5-(exo-3-(5-chloropyrid-3-yl)-endo-3-cyano-8-azabicyclo[3.2.1]oct-8-yl)-1,2,4-thiadiazol-3-yl)methyl)-8-azabicyclo[3.2.1]octane (0.083g).

10

EXAMPLE 6

This Example illustrates an emulsifiable concentrate composition which is readily convertible by dilution with water into a liquid preparation suitable for spraying purposes. The concentrate has the following composition:

	% Weight
Compound No. 1	25.5
SYNPERONIC NP13	2.5
Calcium dodecylbenzenesulphonate	2.5
AROMASOL H	70

EXAMPLE 7

15

This Example illustrates a wettable powder composition which is readily convertible by dilution with water into a liquid preparation suitable for spraying purposes. The wettable powder has the following composition:

	% Weight
Compound No. 13	25.0
Silica	25.0
Sodium lignosulphonate	5.0
Sodium lauryl sulphate	2.0
Kaolinite	43.0

EXAMPLE 8

This Example illustrates a dusting powder which may be applied directly to plants or  
 20 other surfaces and comprises 1% by weight of Compound No. 25 and 99% by weight of talc.

EXAMPLE 9

This Example illustrates a concentrated liquid formulation suitable for application by ultra low volume techniques after mixing with paraffinic diluents.

	% Weight
Compound No. 29	90.0
SOLVESSO 200	10.0

EXAMPLE 10

- 5 This Example illustrates a capsule suspension concentrate which is readily convertible by dilution with water to form a preparation suitable for application as an aqueous spray.

	% Weight
Compound No. 43	10.0
Alkylbenzene solvent (e.g. AROMASOL H)	5.0
Toluene di-isocyanate	3.0
Ethylenediamine	2.0
Polyvinyl alcohol	2.0
Bentonite	1.5
Polysaccharide (e.g. KELTROL)	0.1
Water	76.4

EXAMPLE 11

A ready for use granular formulation:

	% Weight
Compound No. 4	0.5
SOLVESSO 200	0.2
nonylphenol ethoxylate (eg Synperonic NP8)	0.1
Calcium carbonate granules (0.3-0.7 mm)	99.2

EXAMPLE 12

An aqueous suspension concentrate:

	% Weight
Compound No. 8	5.0
Kaolinite	15.0
Sodium lignosulphonate	3.0
nonylphenolethoxylate (eg Synperonic NP 8)	1.5
propylene glycol	10.0
Bentonite	2.0
Polysaccharide (eg Keltrol)	0.1
Bactericide (eg Proxel; Proxel is a registered Trade Mark)	0.1
Water	63.3

EXAMPLE 13

5        This Example illustrates a water dispersible granule formulation.

	% Weight
Compound No. 20	5
Silica	5
Sodium lignosulphate	10
Sodium dioctylsulphosuccinate	5
Sodium acetate	10
Montmorillonite powder	65

EXAMPLE 14

10        This Example illustrates the insecticidal properties of the compounds of formula (I).  
The activity of the compounds of formula (I) was determined using a variety of pests. The  
pests were treated with a liquid composition containing 500 parts per million (ppm) by  
weight of the compound unless otherwise stated. The compositions were made by dissolving  
the compound in acetone and ethanol (50:50) mixture and diluting the solutions with water  
containing 0.05% by weight of a wetting agent sold under the trade name "SYNPERONIC"

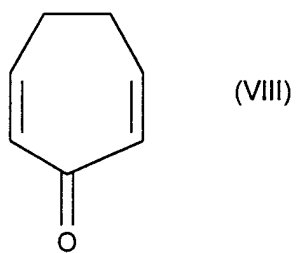
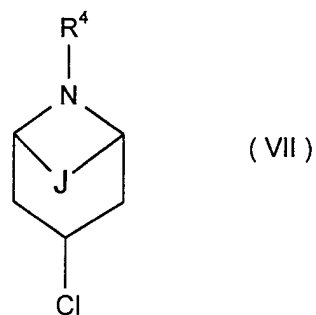
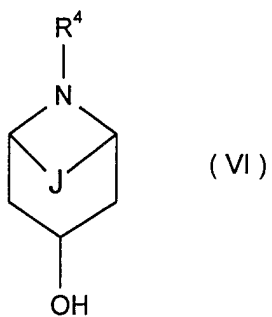
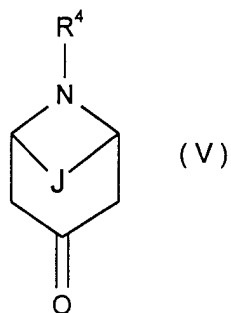
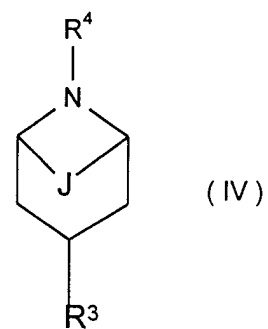
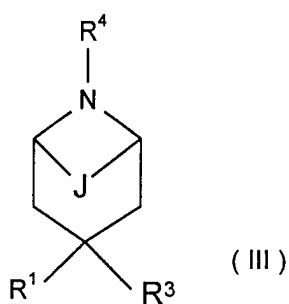
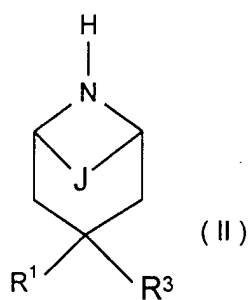
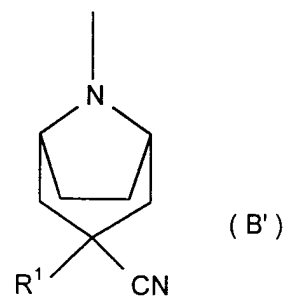
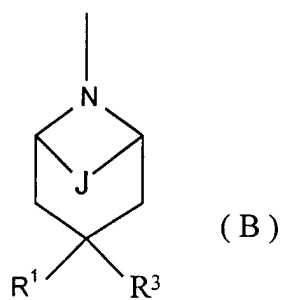
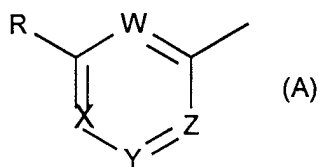
NP8 until the liquid composition contained the required concentration of the compound.

"SYNPERONIC" is a Registered Trade Mark.

The test procedure adopted with regard to each pest was basically the same and comprised supporting a number of the pests on a medium which was usually a substrate, a host plant or a foodstuff on which the pests feed, and treating either or both the medium and the pests with the compositions. The mortality of the pests was then assessed at periods usually varying from two to five days after the treatment.

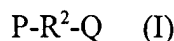
The results of the tests against peach aphid (Myzus persicae) are presented below. The results indicate a grading of mortality (score) designated as A, B or C wherein C indicates less than 40% mortality, B indicates 40-79% mortality and A indicates 80-100% mortality; "-" indicates that either the compound was not tested or no meaningful result was obtained. In this test Chinese cabbage leaves were infested with aphids, the infested leaves were sprayed with the test composition, and the mortality assessed after 3 days. Compound Nos 1 and 2 of Table I gave a mortality score of A.



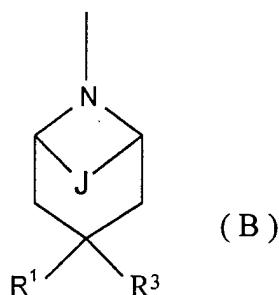
CHEMICAL FORMULAE  
(in description)

CLAIMS

1. A compound of formula (I):



- 5 where each of P and Q is, independently, a group of formula (B):



- wherein J is a bidentate group of formula  $-CH_2-X-CH_2-$  (wherein X is methylene, sulfur or oxygen),  $X'C=CY$  or  $X'WC-CYZ$  (wherein X', W, Y and Z are independently hydrogen, hydroxy, acyloxy, alkoxy, alkylsilyloxy or halogen);  $R^1$  is an optionally substituted phenyl or 5-or 6-membered heterocyclic ring system containing from 1 to 3 heteroatoms individually selected from nitrogen, oxygen and sulfur atoms, and at least one unsaturation (double bond) between adjacent atoms in the ring, said heterocyclic ring being optionally fused to a benzene ring, wherein the substituents, if present, are selected from halogen atoms, cyano, alkyl, alkenyl, alkynyl, alkoxy, haloalkyl, haloalkenyl, alkylthio and alkyl amino groups, any of which groups contain up to six carbon atoms;  $R^2$  is a bidentate linking group and is a substituted or unsubstituted alkylene, alkylenearyl, alkyleneheteroaryl, alkenylene, alkylenearylalkylene, carbonyl or diacyl group, provided that when  $R^2$  is alkenylene or alkylenearylalkylene said group does not have an unsaturated carbon atom bonding directly to the ring nitrogen of formula (B);  $R^3$  is hydrogen, cyano, hydroxy, alkyl, alkoxy, amino, nitro, isocyanato, acylamino, hydroxyalkyl, optionally substituted heteroaryl, alkoxyalkyl, haloalkyl, halohydroxyalkyl, aralkyloxyalkyl, acyloxyalkyl, amidoximido, sulfonyloxyalkyl, aminoalkyl, alkoxycarbonylamino, acylaminoalkyl, cyanoalkyl, imino, formyl, acyl or carboxylic acid or an ester or amide thereof, or alkenyl or alkynyl either of which is optionally substituted by halogen, alkoxy, cycloalkyl, optionally substituted aryl,

optionally substituted heteroaryl or cyano; or an acid addition salt, quaternary ammonium salt or N-oxide derived therefrom.

2. A compound of formula (I) as claimed in claim 1 wherein R<sup>3</sup> is cyano.

3. A compound of formula (I) as claimed in claim 1 or 2 wherein J is CH<sub>2</sub>-CH<sub>2</sub> or CH=CH.

4. A compound of formula (I) as claimed in claim 1, 2 or 3 wherein R<sup>1</sup> is an optionally halogen, C<sub>1-4</sub> alkoxy or cyano substituted phenyl group or an optionally halogen, C<sub>1-4</sub> alkoxy or cyano substituted pyridyl, pyridazinyl or pyrazinyl group.

5. A compound of formula (I) as claimed in claim 1, 2, 3 or 4 wherein R<sup>1</sup> is an optionally halogen substituted pyridyl group.

6. A compound of formula (I) as claimed in any one of the preceding claims wherein R<sup>2</sup> is alkylene containing up to 8 carbon atoms.

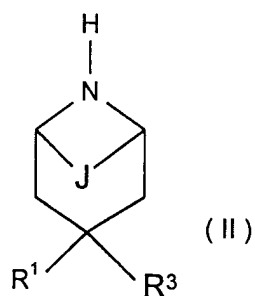
7. An insecticidal, acaricidal or nematocidal composition comprising an insecticidally, acaricidally or nematocidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor.

8. A method of combating and controlling insect, acarine or nematode pests at a locus which comprises treating the pests or the locus of the pests with an effective amount of a compound as claimed in claim 1 or a composition according to claim 7.

9. A method according to claim 8 wherein the pests are insect pests of growing plants.

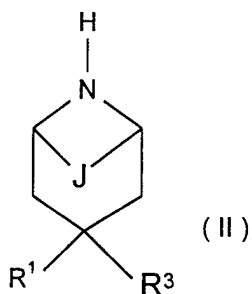
10. A method of preparing a compound of formula (I) as claimed in Claim 1 which comprises:

(a) reacting a compound of formula (II):



with a compound of formula  $L-R^2-L$  where L represents an easily displaceable leaving atom or group, in the presence of a base;

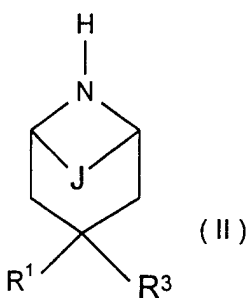
(b) by reductive amination of a compound of formula (II):



5

with a dialdehyde of formula  $OHC-R^5-CHO$ , where  $R^2$  is  $H_2C-R^5-CH_2$ , in the presence of a suitable reducing agent; or,

(c) by treating a compound of formula (II):



10

with a suitable base in the presence of a diacid chloride of formula  $ClOC-R^5-COCl$ , where  $R^2$  is  $OC-R^5-CO$ .

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 97/02987

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07D451/02 A01N43/90

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 25527 A (H. LUNDBECK A/S) 23 December 1993 see examples 1n,1o see page 15; claims 1,2,4,5 ---	1
A	EP 0 216 625 A (THE WELLCOME FOUNDATION LIMITED) 1 April 1987 ---	1-10
A	WO 93 14636 A (DOWELANCO) 5 August 1993 ---	1-10
A	WO 95 03306 A (E.I. DU PONT DE NEMOURS AND COMPANY) 2 February 1995 ---	1-10
A	WO 96 08968 A (DOWELANCO) 28 March 1996 ---	1-10
P,A	WO 96 37494 A (ZENECA LIMITED) 28 November 1996 ---	1-10
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### ° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

28 January 1998

Date of mailing of the international search report

13. 02. 98

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Hartrampf, G

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02987

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	<p>WO 97 43286 A (ZENECA LIMITED) 20 November 1997  see the whole document  -----</p>	1-10

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02987

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9325527 A	23-12-93	AU 671462 B	29-08-96
		AU 4311393 A	04-01-94
		CA 2137811 A	23-12-93
		CZ 9403122 A	13-09-95
		EP 0649407 A	26-04-95
		FI 945808 A	09-12-94
		IL 105858 A	16-10-96
		JP 8503690 T	23-04-96
		NO 944757 A	31-01-95
		SK 152694 A	10-05-95
		US 5658921 A	19-08-97
		US 5684012 A	04-11-97
		ZA 9304031 A	07-01-94
EP 216625 A	01-04-87	AP 66 A	12-12-89
		AT 118776 T	15-03-95
		AU 6302886 A	26-03-87
		AU 603064 B	08-11-90
		AU 6302986 A	26-03-87
		DE 3650240 D	30-03-95
		DE 3650240 T	14-06-95
		DK 452186 A	25-03-87
		DK 452286 A	10-06-87
		EP 0216624 A	01-04-87
		JP 2082394 C	23-08-96
		JP 7121948 B	25-12-95
		JP 62111987 A	22-05-87
		JP 62116585 A	28-05-87
		US 5116862 A	26-05-92
		US 4965257 A	23-10-90
		US 4985582 A	15-01-91
		US 5157029 A	20-10-92
		US 5371075 A	06-12-94
WO 9314636 A	05-08-93	US 5244906 A	14-09-93
		AU 651516 B	21-07-94
		AU 3239693 A	01-09-93
		BR 9205804 A	17-05-94
		CA 2105556 A	24-07-93
		EP 0577788 A	12-01-94

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02987

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9314636 A		JP 6509359 T	20-10-94
WO 9503306 A	02-02-95	AU 7474794 A	20-02-95
WO 9608968 A	28-03-96	US 5393767 A	28-02-95
		AU 7800394 A	09-04-96
WO 9637494 A	28-11-96	AU 5698896 A	11-12-96
		GB 2301819 A	18-12-96
WO 9743286 A	20-11-97	NONE	