



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C07D 213/38, C07F 7/18, C07D 401/06, A61K 31/44, 31/695 // C07D 213/53, 213/61, 213/78</p>	A3	<p>(11) International Publication Number: WO 96/31475</p> <p>(43) International Publication Date: 10 October 1996 (10.10.96)</p>
<p>(21) International Application Number: PCT/US96/05078</p> <p>(22) International Filing Date: 4 April 1996 (04.04.96)</p> <p>(30) Priority Data: 08/419,597 7 April 1995 (07.04.95) US</p> <p>(60) Parent Application or Grant (63) Related by Continuation US 08/419,597 (CIP) Filed on 7 April 1995 (07.04.95)</p> <p>(71) Applicant (for all designated States except US): SIBIA NEUROSCIENCES, INC. [US/US]; 505 Coast Boulevard South, La Jolla, CA 92037-4641 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): COSFORD, Nicholas, D. [GB/US]; Apartment 4-532, 17442 Matinal Road, San Diego, CA 92127 (US). VERNIER, Jean-Michel [FR/US]; 5265 Toscana Way #238, San Diego, CA 92122 (US).</p> <p>(74) Agent: REITER, Stephen, E.; Pretty, Schroeder, Brueggemann & Clark, Suite 2000, 444 South Flower Street, Los Angeles, CA 90071 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), 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).</p> <p>Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> <p>(88) Date of publication of the international search report: 6 February 1997 (06.02.97)</p>	
<p>(54) Title: SUBSTITUTED PYRIDINE DERIVATIVES, THEIR PREPARATION AND THEIR USE AS MODULATORS OF ACETYLCHOLINE RECEPTORS</p>		
<p>(57) Abstract</p> <p>In accordance with the present invention, there are provided compounds having the structure (I), wherein: A, B, N_a, R_a, Z, R², R⁴, R⁵ and R⁶ are defined as in the description. The compounds of the invention displace acetylcholine receptor ligands from their binding sites. Invention compounds may act as agonists, partial agonists, antagonists or allosteric modulators of acetylcholine receptors, and are useful for a variety of therapeutic applications, such as the treatment of Alzheimer's disease and other disorders involving memory loss and/or dementia (including AIDS dementia); disorders of attention and focus (such as attention deficit disorders); disorders of extrapyramidal motor function such as Parkinson's disease, Huntington's disease, Gilles de la Tourette syndrome and tardive dyskinesia; mood and emotional disorders such as depression, panic, anxiety and psychosis; substance abuse including withdrawal syndromes and substitution therapy; neuroendocrine disorders and dysregulation of food intake, including bulimia and anorexia; disorders of nociception and control of pain; autonomic disorders including dysfunction of gastrointestinal motility and function such as inflammatory bowel disease, irritable bowel syndrome, diarrhea, constipation, gastric acid secretion and ulcers; pheochromocytoma; cardiovascular dysfunction including hypertension and cardia arrhythmias, comedication in surgical procedures, and the like.</p> <div style="text-align: center;"> <p style="text-align: right;">(I)</p> </div>		

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GA	Gabon			VN	Viet Nam

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 96/05078

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C07D213/38 C07F7/18 C07D401/06 A61K31/44 A61K31/695
 //C07D213/53,C07D213/61,C07D213/78

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 C07F

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	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 69, October 1947, pages 2461-2466, XP000576079 DOERING W.E. & WEIL R.A.N.: "Electrophilic reactions of 2- and 4-vinylpyridines" see page 2463, compound XXII see page 2465, column 2 - page 2466, column 2	1,2,6, 9-11,13, 21,37
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	ACTA CHEMICA SCANDINAVICA, vol. 17, no. 6, 1963, pages 1735-1742, XP000576072 HAGLID F. & WELLINGS I.: "Synthetic analogues of nicotine. III" see page 1737, compound 7 see table 2	1,2, 6-11,13, 24,42,43

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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

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Date of the actual completion of the international search 29 November 1996	Date of mailing of the international search report 23. 12. 96
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Hartrampf, G
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INTERNATIONAL SEARCH REPORT

International Application No
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X	NL,A,6 401 902 (CHARLES E. FROSST & CO.) 30 August 1965 see claims 1,3,7,13-15; examples 4,10-12 ---	1,2, 9-11,13, 42
X	US,A,3 313 822 (MELTZER R.I.) 11 April 1967 see claims 1,3,6; examples 3,4 ---	1,2, 9-11,13, 42
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X	FR,A,2 255 904 (BEIERSDORF AKTIENGESELLSCHAFT) 25 July 1975 see example 3; table II ---	1,2, 9-11,13, 42
X	ARCHIV DER PHARMAZIE (WEINHEIM GER.), vol. 320, no. 7, 1987, pages 647-654, XP002009425 HOLZGRABE U.: "Cer(IV)sulfat-Oxidationen: Intramolekulare Cyclisierung von N-Benzyl-.beta.-aminoketonen zu 4-Benzoyl-1,2,3,4-tetrahydroisochinolinen" see page 649, compound 3h ---	1,2,6, 9-11,13, 36
X	HETEROCYCLES, vol. 24, no. 6, 1986, pages 1687-1698, XP000575751 SECOR H.V. & SEEMAN J.I.: "The preparation of "elongated" nicotine analogues" see the whole document ---	1,2, 7-11,13
X	EP,A,0 567 250 (R.J. REYNOLDS TOBACCO COMPANY) 27 October 1993 see the whole document ---	1,2,7,8, 10,11, 13,42,43
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INTERNATIONAL SEARCH REPORT

 International Application No
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X	HELVETICA CHIMICA ACTA, vol. 45, no. 3, 2 May 1962, pages 1018-1026, XP000608985 NAEF K.M. & SCHALTEGGER H.: "116. Enamine und Amide 3-substituierter Pyridinderivate" see the whole document ---	1,9-11, 13
X	AGRICULTURAL AND BIOLOGICAL CHEMISTRY, vol. 32, no. 1, January 1968, pages 747-752, XP000609497 SOEDA Y. & YAMAMOTO I.: "Studies on nicotinoids as an insecticide. Part VI. Relation of structure to toxicity of pyridylalkylamines" see figure 1-4, page 750 ---	1,9-11, 13
X	DE,A,22 20 333 (AB HÄSSLE) 31 January 1974 see claims 1,5,10 ---	1,9-11, 13,42
X	JOURNAL OF ORGANIC CHEMISTRY, vol. 46, no. 17, 14 August 1981, pages 3479-3483, XP000608977 BÄCKVALL J.-E. ET AL.: "Synthesis of 3-aryl-3-pyridylallylamines related to zimelidine via palladium-catalyzed amination" see scheme I, compounds 4a - 4f see page 3482; table IV ---	1,9-11, 13
X	CHEMISTRY OF HETEROCYCLIC COMPOUNDS, vol. 19, no. 5, November 1983, pages 518-524, XP000609295 KOIKOV L.N. ET AL.: "Reactivities of isomeric (1-dimethylaminovinyl)pyridines, reaction with sulfene" see table 1 ---	1,9-11, 13
X	HETEROCYCLES, vol. 22, no. 11, November 1984, pages 2475-2478, XP000609297 ISHIKURA M. ET AL.: "A novel synthesis of 3- and 4-alkenylpyridines" see page 2476; table 1 ---	1,2, 7-11,13, 25,26, 54,55

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 1, 1974, pages 2671-2672, XP000608980 STRADI R. ET AL.: "Enamines. Part XXXVIII. Configurations of 1-aryl-1-dialkylaminopropenes" see compounds I _k and I _l see page 2672; table 1 see compounds I _l c and I _l d see page 2672; table 2 ---	1,2, 7-11,13
X	JOURNAL OF MEDICINAL CHEMISTRY, vol. 31, no. 5, May 1988, pages 913-919, XP000608983 HÖGBERG T. ET AL.: "Homoallylic amines related to zimeldine. A comparative study on neuronal serotonin and norepinephrine reuptake based on conformational analysis" see the whole document ---	1,9-11, 13,42
X	EP,A,0 559 413 (R.J. REYNOLDS TOBACCO COMPANY) 8 September 1993 see the whole document ---	1,2, 9-11,13, 42,43
X	C.R. HEBD. SEANCES ACAD. SCI., vol. 252, 1961, pages 2416-2417, XP000609064 MIOCQUE M. & GAUTIER J.-A.: "Sur une nouvelle voie d'accès aux pyridylalcynes" see the whole document ---	1,9-11, 13
X	ACTA PHARMACEUTICA SUECICA, vol. 1, 1964, pages 237-245, XP000609362 DAHLBOM R. ET AL.: "Acetylene compounds of potential pharmacological value" see page 241; table 1 ---	1,7-11, 13,42,43
X	CHEMICAL ABSTRACTS, vol. 71, no. 17, 27 October 1969 Columbus, Ohio, US; abstract no. 81101z, KOTLYAREVSKII I.L. ET AL.: "Synthesis and some reactions of .beta.-ethynylpyridine" page 368; column 1; XP002019874 see abstract & IZV. SIB. OTD. AKAD. NAUK SSSR, SER. KHIM. NAUK, no. 2, 1969, pages 111-115, ---	1,7-11, 13
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INTERNATIONAL SEARCH REPORT

Inter. Application No

PCT/US 96/05078

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	COLLECTION CZECHOSLOVAK. CHEM. COMMUN., vol. 54, no. 4, April 1989, pages 1067-1081, XP000608975 SILHANKOVA A. ET AL.: "Mannich and Grignard reaction of some N-(2-propynyl)azaheterocycles" see compounds Xg and Xic see page 1071 ---	1,7-11, 13
X	US,A,2 194 567 (RENSHAW R.R. & DREISBACH P.F.) 26 March 1940 see the whole document ---	1,7-11, 13,42
X	GB,A,945 824 (E. MERCK AKTIENGESELLSCHAFT) 8 January 1964 see the whole document ---	1,7-11, 13,42
X	DE,A,18 02 777 (HEXACHIMIE S.A.) 19 June 1969 see the whole document ---	1,7-11, 13,42,43
X	DE,A,23 23 354 (CASSELLA FARBWERKE MAINKUR AG) 6 December 1973 see the whole document ---	1,9-11, 13,42
X	CH,A,550 794 (HEXACHIMIE S.A.) 28 June 1974 see the whole document ---	1,7-11, 13,42,43
X	US,A,4 009 174 (CLUZAN R. & KATZ L.) 22 February 1977 see the whole document ---	1,7-11, 13,42
X	DE,A,26 35 961 (AB GRINDSTEDVAERKET) 3 March 1977 see the whole document ---	1,9-11, 13,42
X	DE,A,27 07 135 (PARCOR) 25 August 1977 see the whole document ---	1,7-11, 13,42
X	DE,A,27 16 125 (YOSHITOMI PHARMACEUTICAL INDUSTRIES, LTD.) 27 October 1977 see claims 1-3,7,9 ---	1,9-11, 13,42
X	EP,A,0 571 139 (R.J. REYNOLDS TOBACCO COMPANY) 24 November 1993 see the whole document -----	1,7-11, 13,42,43

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 96/05078

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
PLEASE SEE ATTACHED SHEET ./.

2. Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
PLEASE SEE ATTACHED SHEET ./.

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

PLEASE SEE ATTACHED SHEET ./.

* *

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/210

Lack of conciseness

Finally, it is stressed that patent claims must be clear and concise (cf. Article 6 PCT) in order to enable potential users to ascertain, without undue burden, let alone recourse to litigation, whether their planned commercial use is likely to infringe the patent monopoly.

The definition of the compounds of the Markush formula (I) is too general and/or encompasses too broad a range of different chemical groups, only partly supported by examples given in the descriptive part of the application. Claim 1 and subsequent claims are considered to be insufficiently substantiated by the description.

The vast number of theoretically conceivable compounds resulting from a Claim 1 drafted in such an ambiguous way precludes a comprehensive search. Furthermore there are several contradictions between the description and the claims since several compounds explicitly made and claimed *per se* are excluded by provisos in Claim 1, which additionally renders the scope of the claims ambiguous.

Guided by the inventive concept as disclosed in the descriptive part of the present application the search has been limited to the examples, cf. Articles 6 and 15 PCT, Rule 33 PCT and the PCT Search Guidelines chapter III, 3.6, 3.7 and 3.12 and chapter VIII, 2.

Despite the above limitation the search revealed too many relevant documents and/or compounds so that the search report shall not be considered complete, cf. PCT Search Guidelines chapter III, 2.

Remark:

Although Claims 44 to 48 are directed to a method of treatment of (diagnostic method practised on) the human/animal body the search has been carried out and based on the alleged effects of the compound/composition.

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1. Claims: (1, 2, 4, 6-15 (all part.)), 16-24, 27, 29-41, (42, 43 (both part.)), 49, (50, 51 (both part.)), 52 and 56 (part.).
2. Claims: (1, 2 (both part.)), 3, (4, 6-15 (all part.)), 25, 26, (42, 43, 50, 51 (all part.)), 54, 55 and 56 (part.).
3. Claims: (1, 4, 6-15, 42, 43, 50, 51 and 56 (all part.))
4. Claims: (1, 4 (both part.)), 5 (6-15 (all part.)), 28, (42, 43, 50, 51 (all part.)), 53 and 56 (part.).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/05078

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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