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European Patent Office
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Search Strategy in Medicinal Chemistry

(with Examples on Polymorphic Forms)



Jean-Dominique Moriggi Dir. 1492, Pure and Applied Organic Chemistry 5/11/2014

Overview

Search and retrieval of prior art for patents

1. How do EPO examiners work?
2. External database (STN)
3. Internal database (EPODOC / ESPACENET)
4. Other external databases (Reaxys, Integrity)
5. Classification

Basic search principles

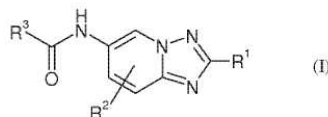
- Search should be broad enough so that no relevant information is missing
- Search effort must stay within reasonable bounds in terms of time and resources
- Search is a dynamic process: adapt the strategy to the current case, the current needs and the current results

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Search specificity of pharmaceutical applications

- Specificity of chemical/pharmaceutical applications:
 - Chemical formula (vs. keywords)
 - Classification system

The invention is concerned with triazolopyridine compounds of formula (I) wherein R¹, R² and R³ are as defined in the description and in the claims, as well as physiologically acceptable salts thereof. These compounds inhibit PDE10A and can be used as medicaments.



Structural Search in an external database (Reaxys):
64 compounds in 7 citations
(6 patents + 1 NPL)

[SS 1] ..fi epodoc

Database: EPODOC

[EPODOC: SS 1] /c c07d471/04

Results in EPODOC **101.109**

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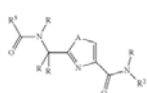
4

Search specificity of pharmaceutical applications

CLAIMS (22)

We claim:

1. A compound of Formula III



wherein, independently for each occurrence,

R^2 is substituted or unsubstituted aryl or substituted or unsubstituted heteroaryl;

A is $-O-$, $-S-$, or $-NR-$;

R is $-H$, or alkyl, and

R^3 is substituted or unsubstituted heteroaryl.

1 structural search

vs.

(at least) 3 classes

C07D403/12

C07D413/12

C07D417/12

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Successful search strategy

- Stage 1: **Coarse filter**
Develop search statements and screen the databases to select a subset of documents most likely to be relevant
- Stage 2: **Fine filter**
Read the original documents to identify the most relevant and discard the others. Compare the invention with the documents
- Further searching necessary?

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Stage 1: Coarse filter

1. Harvest information from the application and identify key search concepts
2. Analyse the key search concepts and identify synonyms, classes, etc.
3. Formulate search statements, query relevant databases
4. Collect documents which might be relevant

For which purpose?

- First medical use of novel active pharmaceutical ingredients; novel polymorphic forms

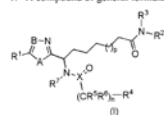
Claims

1. A polymorphic form C of Efavirenz **characterized by** an X-ray powder diffraction pattern which comprises characteristic 2 θ values at: 7.1, 7.3, 11.0, 13.8, 14.2, 14.6, 19.1, 20.9, 21.2, 24.5 and 24.9 ± 0.2 degrees 2 θ .

- Second (and further) medical use of a known active pharmaceutical ingredients

CLAIMS

1. A compound of general formula (I):



wherein:

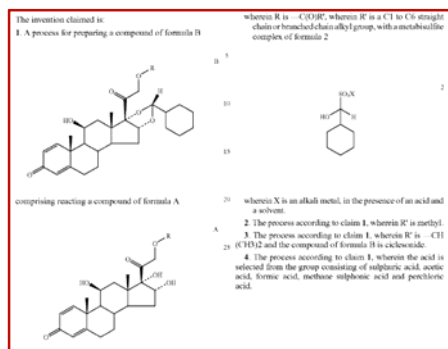
X is C or S=O;

[...]

and pharmaceutically acceptable salts, tautomers, stereoisomers thereof, for use in the treatment of parasitic diseases.

For which purpose?

- Chemical process (alternative or improved process of a process for the preparation of a known compound)



- Novelty
- Inventive step

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Crystalline forms of rifaximin (description)

CLAIMS

1. A crystalline form κ of Rifaximin, characterised by a powder XRD spectrum with peaks at values of the angle 2θ of 5.3°, 6.8°, 7.8°, 8.5°, 9.3°, 10.1°, 10.3°, 12.1°, 12.7°, 13.1°, 14.4°, 17.1°, 17.9°, 18.3°, 20.9°, 21.4°, 22.1° and 20.3° and

Patent application EP 1557421 A1 describes three polymorphs of Rifaximin. The first form, designated α , has a powder X-ray diffraction (XRD) spectrum which presents peaks at the values of angle 2θ of 6.6°, 7.4°, 7.9°, 8.8°, 10.5°, 11.1°, 11.8°, 12.9°, 17.6°, 18.5°, 19.7°, 21.0°, 21.4° and 22.1°. The second form, designated β , has a powder X-ray diffraction (XRD) spectrum with peaks at the values of angle 2θ of 5.4°, 6.4°, 7.0°, 7.8°, 9.0°, 10.4°, 13.1°, 14.4°, 17.1°, 17.9°, 18.3° and 20.9°. Finally, the third polymorphic form cited in this application, designated γ , has a lesser degree of crystallinity and has a powder X-ray diffraction (XRD) spectrum with peaks at the values of angle 2θ of 5.0°, 7.1° and 8.4°.

Patent application WO 2006/094662 A1 describes two polymorphic forms of Rifaximin, designated δ and ϵ respectively; the first has a water content within the range from 2.5 to 6% by weight (preferably from 3 to 4.5%), and a powder XRD

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Crystalline forms of rifaximin (STN)

CLAIMS

1. A crystalline form κ of Rifaximin, characterised by a powder XRD spectrum with peaks at values of the angle 2θ of 5.3°, 6.8°, 7.8°, 8.5°, 9.3°, 10.1°, 10.3°, 12.1°, 12.7°, 13.4°, 13.7°, 14.6°, 15.3°, 15.8°, 16.4°, 16.9°, 17.7°, 18.0°, 18.8°, 19.2°, 19.7°, 20.3° and 22.1°.

```
? rifaximin/CN
L1          1 RIFAXIMIN/CN
```

```
?      80621-81-4/rn
L1          1 80621-81-4/RN
```

European Patent Office

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Crystalline forms of rifaximin (STN)

→ ? ..fi caplus
WARNING :On STN ,your queries are not renumbered at file switch

→ ? l1 and (polymorph+ or cryst+ or recryst+)

484 L1
342134 POLYMORPH?
2811351 CRYST?
147977 RECRYST?

L2 35 L1 AND (POLYMORPH? OR CRYST? OR RECRYST?) (amorph+)

(L) operator

```
? E polymorphism/CT
```

#	FREQUENCY	AT	TERM
E1	0	1	POLYMORPHICA/CT
E2	0	1	POLYMORPHOIDES/CT
E3	2289	3 -->	POLYMORPHISM/CT
E4	5261	2	POLYMORPHISM (CRYSTAL)/CT
E5	0	3	POLYMORPHISM (CRYSTAL) (L) ALLOTROPY/CT
E6	0	2	POLYMORPHISM (CRYSTAL) (L) DIMORPHISM/CT
E7	0	2	POLYMORPHISM (CRYSTAL) (L) ENANTIOTROPY/CT
E8	0	2	POLYMORPHISM (CRYSTAL) (L) MEMOTROPY/CT
E9	0	2	POLYMORPHISM (CRYSTAL) (L) PSEUDOPOLYMORPHISM/CT
E10	11	2	POLYMORPHISM (CRYSTAL) , ALLOTROPY/CT
E11	7	2	POLYMORPHISM (CRYSTAL) , DIMORPHISM/CT
E12	0	2	POLYMORPHISM (L) DIMORPHISM/CT

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Crystalline forms of rifaximin (STN)

tetracyanoethanesulfonic acid in the form of a light yellow powder, M. P. 197–198° C. A sample is recrystallized from water to give white needles, M. P. 198–199° C.
Analysis.—Calcd. for $C_{22}H_{32}N_6SO_3$: C, 61.39; H, 6.34; N, 16.52; S, 6.30. Found: C, 61.18; H, 6.49; N, 16.52, 16.40; S, 6.41, 6.22.

```
? L1
L2      685 L1
? L1/prep/form
      685 L1
      6095157 PREP/RL
      26 L1/PREP
          (L1 (L) PREP/RL)
      685 L1
      1038062 FORM/RL
          1 L1/FORM
          (L1 (L) FORM/RL)
L3      27 L1/PREP OR L1/FORM
?
```

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Crystalline forms of rifaximin (STN)

FILE 'REGISTRY'

L1 1 80621-81-4/RN

FILE 'CAPLUS'

L4 681 L1

L5 61 L4 AND (POLYMORPH? OR CRYSTAL? OR RECRYSTAL?) ←

L9 34 L4 (L) (POLYMORPH? OR CRYSTAL? OR RECRYSTAL?)

L7 4 L4 AND (E3 OR E4)

L8 26 L1/PREP ←

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Crystalline forms of rifaximin (Espacenet / Epodoc)

[illegible]

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Crystalline forms of rifaximin (Espacenet / Epodoc)



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Office enquiries
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Info: WO2012/156951 (A1)

- Bibliographic data: WO2012/156951 (A1) ▼
- Description
- Claims
- Abstract
- Cited documents
- Citing documents
- IPC Classifications
- INPADOC patent family

Bibliographic data: WO2012/156951 (A1) — 2012-11-22

[In my patents list](#) > [EP Register](#) > [Process data error](#) > [Print](#)

★ POLYMER OF RIFAXIMIN AND PROCESS FOR THE PREPARATION THEREOF

Page bookmark	WO2012156951(A1) : POLYMERS OF RIFAXIMIN AND PROCESS FOR THE PREPARATION THEREOF
Inventor(s)	VIGANO ENRICO JT; MOLteni RENATO JT; LANFRANCOSI SIMONA JT; MORRICI MASSIMO/LINO JT; GATTI FABIO JT;
Applicant(s)	A.M.S.A. FARMACIAINTERIE S.R.L. ET AL. B.P. A JT; VIGANO ENRICO JT; MOLteni RENATO JT; LANFRANCOSI SIMONA JT; MORRICI MASSIMO/LINO JT; GATTI FABIO JT;
Classification:	- International: A61K13/06 ; A61P06/00 ; G01C4/002 - Cooperative: A61K13/038 ; C07D400/02
Application number	WO/2012/25015 29.12.05/18
Priority number(s)	(IT)211080089 09.12.05/18
Also published as:	US2012137873(A1); US2012130345(A1); US2010400415(A1); IT080210080(A1); EP2210015(A1); CN102110809

Abstract of WO2012/156951 (A1)

Translate this text into [or print it](#) [or download it](#) (powered by Google Translate)

The present invention relates to a new polymorph of Rifaximin, designated "7", and to a process for the preparation thereof. Under certain aspects, the invention also relates to pharmaceutical compositions comprising an effective amount of the polymorphic form "7" of Rifaximin and a pharmaceutically acceptable carrier and its uses in the treatment of gastrointestinal conditions.



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Crystalline forms of rifaximin (Espacenet / Epodoc)

4. Documented data in relation to WGS20170001 (4)						
Sort by: <u>Priority date</u> Sort order: <u>Descending</u> <u>Sort</u>						
International search relation						
A. <u>Technological features</u>						
Technical assessments for their production and use thereof of mechanical assemblies						
Inventor: WILCOOM GUEPPEE (C) CARPENA MANUELA (J)	Applicant: ALFA ROMEOFINANCIA SPA (PT)	EPC: G12D18932	IPC: A13N13708 A13N134185 A13N134183 (+)	Publication info: EP 1708103 (A1) 2016-04-06 US 9,696,985 (B2) 2016-06-16	Priority date: 2015-07-27	
B. <u>Embodiments</u>						
Technical assessments for their production and use thereof of mechanical assemblies						
Inventor: WILCOOM GUEPPEE (C) CARPENA MANUELA (J)	Applicant: ALFA ROMEOFINANCIA SPA (PT)	G12D18932	A13N13708 A13N134185 G12C18902 (+)	EP 1708103 (A1) 2016-04-06 EP 1708103 (A1) 2016-04-06 EP 1708103 (A1) 2016-04-06	Priority date: 2015-07-27	
C. <u>Details</u>						
MECHANISM AND SHAFTS THEREOF						
Inventor: GILBERT AUREN (S) BENO CONGOLI (S) (+)	Applicant: GILBERT AUREN (S) BENO CONGOLI (S) (+)	G12D18932	A13N13708 A13N134187 (+)	EP 1708103 (A1) 2016-04-06 US 9,696,985 (B2) 2016-03-28	Priority date: 2016-03-25	
D. <u>FORMS OF MECHANISM AND SHAFTS THEREOF</u>						
Inventor: GILBERT AUREN (S) BENO CONGOLI (S) (+)	Applicant: GILBERT AUREN (S) BENO CONGOLI (S) (+)	G12D18932	G12C18902 A13N13708 A13N134187 (+)	EP 1708103 (A1) 2016-04-06 US 9,696,985 (B2) 2013-10-16	Priority date: 2016-03-25	
Parents linked by the applicant						
B. <u>Embodiments</u>						
Technical assessments with mechanical analysis						
Inventor: MARCO EGGO MONTICONE LAURETH	Applicant: ALFA ROMEOFINANCIA SPA (PT)	G12D18932	A13N134185 A13N134183 G12C18902 (+)	US 9,696,985 (A1) 1980-07-27 US 9,696,985 (A1) 1980-07-27	Priority date: 1980-07-27	
A. <u>Explanatory forms of elements or assemblies</u>						
Technical assessments of their production and use thereof of mechanical assemblies						
Inventor: WILCOOM GUEPPEE (C) CARPENA MANUELA (J)	Applicant: ALFA ROMEOFINANCIA SPA (PT)	G12D18932	A13N13708 A13N134185 A13N134183 (+)	EP 1708103 (A1) 2016-04-06 US 9,696,985 (B2) 2016-06-16	Priority date: 2015-07-27	
B. <u>MECHANICAL PROFILES OF MECHANISM PROFILES FOR THEIR PRODUCTION AND USE THEREOF IN THE MECHANISM</u>						
Inventor: WILCOOM GUEPPEE (C) CARPENA MANUELA (J)	Applicant: ALFA ROMEOFINANCIA SPA (PT)	G12D18932	A13N13708 A13N134185 A13N134183 (+)	EP 1708103 (A1) 2016-04-06 US 9,696,985 (B2) 2016-06-16	Priority date: 2015-07-27	
C. <u>FORMS OF MECHANISM AND SHAFTS THEREOF</u>						
Inventor: GILBERT AUREN (S) BENO CONGOLI (S) (+)	Applicant: GILBERT AUREN (S) BENO CONGOLI (S) (+)	G12D18932	A13N13708 A13N134187 (+)	EP 1708103 (A1) 2016-04-06 US 9,696,985 (B2) 2016-03-28	Priority date: 2016-03-25	

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Crystalline forms of rifaximin (Espacenet / Epodoc)

[SS 1] ..fi epodoc

Database: EPODOC

[EPODOC: SS 1] RIFAXIMIN

Results in EPODOC 425

[SS 2] ..stat c

STAT C

#		..STAT C	FREQ	/CCA /CCI /CQA /CQI /CUA /CUI	DESCRIPTION
1	185	C07D498/22			In which the condensed system contains four or more hetero rings
2	144	A61K31/437			A61K31/437 the heterocyclic ring system containing a five-membered ring having nitrogen as a ring hetero atom, e.g. indolizine, beta-carboline
3	67	A61K31/44			A61K31/44 Non condensed pyridines; Hydrogenated derivatives thereof
5	55	A61K9/2054			A61K9/2054 {Cellulose; Cellulose derivatives, e.g. hydroxypropyl methylcellulose}
5	45	A61K9/1652			A61K9/1652 {Polysaccharides, e.g. alginate, cellulose derivatives; Cyclodextrin}
6	40	A61K9/5026			A61K9/5026 {obtained by reactions only involving carbon-to-carbon unsaturated bonds, e.g. polyvinyl pyrrolidone, polyacrylates}
7	34	A61K31/395			A61K31/395 .. having nitrogen as a ring hetero atom, e.g. guanethidine, rifamycins
8	34	A61K45/06			A61K45/06 .. Mixtures of active ingredients without chemical characterisation, e.g. antiphototics and cardiaca
9	31	A61K9/1635			A61K9/1635 {obtained by reactions only involving carbon-to-carbon unsaturated bonds, e.g. polyvinyl pyrrolidone, polyacrylates}
10	31	A61K9/2027			A61K9/2027 {obtained by reactions only involving carbon-to-carbon unsaturated bonds, e.g. polyvinyl pyrrolidone, polyacrylates}
11	30	A61K9/2866			A61K9/2866 {Cellulose; Cellulose derivatives, e.g. hydroxypropyl methylcellulose}
12	30	C07D498/18			C07D498/18 Bridged system
13	26	A61K47/10			A61K47/10 Alcohols; Phenols; Salts thereof, {e.g. glycerol; Polyethylene glycol
					; Poloxamers; PEG/POE alkyl ethers

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Crystalline forms of rifaximin (Espacenet / Epodoc)

Advanced search

Select the collection you want to search in: "Database" (filter by published applications from 00 countries)

Enter your search terms: CTRL+ENTER expands the field you are in

Enter keywords in English

Title: people and bicycle

Title or abstract: fat

(Author and coauthor) or Inventor or contributor

Enter numbers with or without country code

Publication number: WO0200014320

Application number: DE1999100109A

Priority number: WO199902619325

Enter one or more dates or date ranges

Publication date: yyyy-mm-dd

Enter names of one or more persons/organizations

Applicant(s): Institut Pasteur

Inventor(s): Smith

Enter one or more classification symbols

CPC: C02F60/00

IPC: H03M1/12

OK Search

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Crystalline forms of rifaximin (Espacenet / Epodoc)

[illegible]

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Crystalline forms of rifaximin (Espacenet / Epodoc)

- look for the recent applications from the same applicant, form the same inventor(s)
- look for applications having the same words in the title

Successful search strategy

- Stage 1: **Coarse filter**
Develop search statements and screen the databases to select a subset of documents most likely to be relevant
- Stage 2: **Fine filter**
Read the original documents to identify the most relevant and discard the others. Compare the invention with the documents
- Further searching necessary?

Stage 2: **Fine filter**

- Study documents in detail
- Do it methodically!

Successful search strategy

- Stage 1: **Coarse filter**
Develop search statements and screen our databases to select a subset of documents most likely to be relevant.
- Stage 2: **Fine filter**
Read the original documents to identify the most relevant and discard the others. Compare the invention with the documents.
- **Further searching necessary?**

Continue search yes/no?

- How successful already?
- How much time spent/left?
- How many databases tried?
- How many queries tried?
- How likely is future success?

Further searches

- Modify query
 - **less** restrictive queries
 - **more** restrictive queries
- Citation hopping

Modify query

CLAIMS

1. A crystalline form κ of Rifaximin, characterised by a powder XRD spectrum with peaks at values of the angle 2θ of 5.3°, 6.8°, 7.8°, 8.5°, 9.3°, 10.1°, 10.3°, 12.1°, 12.7°, 13.4°, 13.7°, 14.6°, 15.3°, 15.8°, 16.4°, 16.9°, 17.7°, 18.0°, 18.8°, 19.2°, 19.7°, 20.3° and 22.1°.

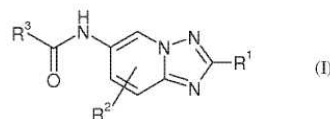
?	80621-81-4/rn
L1	1 80621-81-4/RN

?	80621-81-4/crn
L2	21 80621-81-4/CRN

noise or further relevant documents?

Modify query

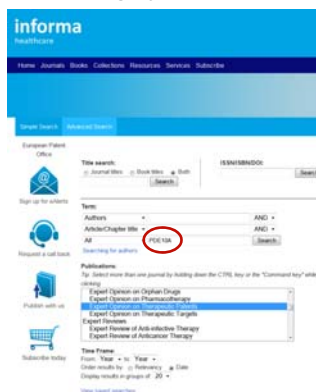
The invention is concerned with triazolopyridine compounds of formula (I) wherein R¹, R² and R³ are as defined in the description and in the claims, as well as physiologically acceptable salts thereof. These compounds inhibit PDE10A and can be used as medicaments.



- Search a broader chemical structure in Registry to find documents potentially relevant not only for novelty but for inventive step as well
- Combine with keywords in Chemical Abstract (receptor, diseases)
- Or do the opposite approach: search a disease first and a structure within said set

Modify query

- Think of bioisosterism
- Look for reviews on a particular patent, integrity, Expert Opinion



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Citation hopping

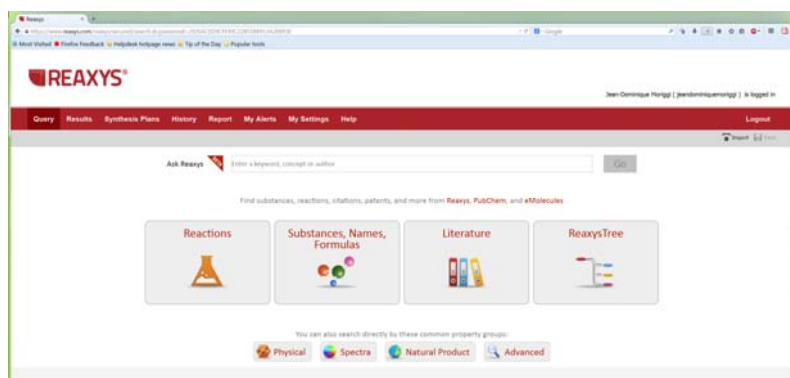
If possible, use regularly and iteratively until no further new or interesting documents turn up

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Reaxys

Reaxys @ www.reaxys.com covers 400 journals and chemistry patents with the International Patent Classes C07, A61K, A01N and C09B



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Reaxys - Compounds

European Patent Office

32

Reaxys – Chemical process

European Patent Office

33

Reaxys – Biological activity

European Patent Office

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Integrity

- Integrity @ <https://integrity.thomson-pharma.com> encompasses essential information on over 380,000 bioactive compounds, 24,000 synthesis schemes, 8,000 companies and research institutions, etc.
- Patent offices covered include WO, EP, US, JP, CN, KR, and IN.

Integrity – Chemical process

[illegible]

Integrity – Biological activity

Quick Search Results

https://integrity.thomson-pharma.com/integrity/umlala

Most Visited Firefox Feedback Helpdesk homepage news TIS

THOMSON REUTERS
Integrity™

Knowledge Areas Quick Search PDE4

You have entered the Quick Search feature. Click one of the Knowledge Areas to obtain information related to the Knowledge Area you are in, click the adjacent list

Results for "PDE4"

Design & Biology 3318

Biomarker 3

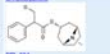
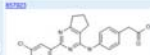
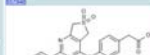
Literature 1291

Deposited Synthesis 1

Pharmacokinetics/ Pharmacodynamics 1

Competition & Research Collaborations 1

Experimental Models 4

WO	Discontinuation	Combination Products	Antifine Chronic obstructive pulmonary disease (COPD)	Chemical Structure
WO 2014/028612 WO 2014/028685 (Pfizer Inc.)	Autism vaccine compounds	Drug Substances	Allegri Anxiety Chronic obstructive pulmonary disease (COPD) Multiple sclerosis Parkinson's disease Schizophrenia	
WO 2014/179471 WO 2014/179482 (Grünenthal GmbH)	1,4-bis(4-substituted phenyl)pyrimidine compounds as PDE4 inhibitors	Drug Substances	Antifine Chronic obstructive pulmonary disease (COPD) Dermatitis, atopic Inflammatory bowel disease Psoriasis Rheumatoid arthritis Rheitis, atopic	
WO 2014/179471 WO 2014/179482 (Grünenthal GmbH)	Novel substituted pyrimidine compounds	Drug Substances	Antifine Chronic obstructive pulmonary disease (COPD) Dermatitis, atopic Inflammatory bowel disease Psoriasis Rheumatoid arthritis Rheitis, atopic	

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Classification

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

(19) World Intellectual Property Organization

International Bureau

(43) International Publication Date

31 January 2013 (2013.01)

WIPO PCT

(8) International Publication Number

WO/2013/014770 A1

(51) International Patent Classification

C02F 1/28 (2006.01) A61P 1/00 (2006.01)

C02F 1/32 (2006.01) A61K 01/28 (2006.01)

C02F 1/38 (2006.01) A61K 01/30 (2006.01)

C02F 1/42 (2006.01) A61K 01/42 (2006.01)

C02F 1/44 (2006.01) A61K 01/44 (2006.01)

C12P 2/02 (2006.01)

(21) International Filing Date

24 July 2012 (2012.07.24)

(52) Filing Language

English

(53) Publication Language

English

(54) Priority Data

60/257,249 filed 27 July 2013 (US 2013/072,499 A1)

Applicant: *et al.* 24 July 2013 (US 2013/072,499 A1)
Inventor: *et al.* 24 July 2013 (US 2013/072,499 A1)

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C07D: heterocyclic compounds

A61K31: medicinal preparations containing organic active ingredients

(A61P: specific therapeutic activity of chemical compounds or medical preparations)

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Classification

- 1991: all documents classified via EC codes according to European Classification only. Additional indexing system of "In Computer Only" codes (ICO codes) was also developed
- 01 January 2013:** EPO replaced EC and ICO by a joint classification system co-owned with USPTO and called the Cooperative Patent Classification (CPC)
- The structure of the **CPC Scheme and Definitions** is generally similar to that of the **IPC**
- Unless otherwise stated, CPC structure, rules and principles are identical to the IPC ones
- The general policy of CPC is to follow the current IPC and to progressively reduce any divergence between the two systems

Classification

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The text of CPC

Examples

? ..fi CPC
? /cc A01B
? ..li
? /cch A01
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■ Internet

PDF versions of the CPC scheme and definitions are available on the official page of the CPC:

<http://www.cooperativepatentclassification.org/cpcSchemeAndDefinitions/table.html>

The CPC can also be searched and browsed on Espacenet:

<http://worldwide.espacenet.com/classification>

1/1	© CPC / EPO
CC	- C07D411/00
TI	- Heterocyclic compounds containing two or more hetero rings, at least one ring having oxygen and sulfur atoms as the only ring hetero atoms
(SS 4)	/cch C07D411/00
Results in CPC 7	
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1/7	© CPC / EPO
CC	- C07D411/02
TI	- containing two hetero rings
2/7	© CPC / EPO
CC	- C07D411/04
TI	- directly linked by a ring-member-to-ring-member bond
3/7	© CPC / EPO
CC	- C07D411/05
TI	- linked by a carbon chain containing only aliphatic carbon atoms
4/7	© CPC / EPO
CC	- C07D411/08
TI	- linked by a carbon chain containing alicyclic rings
5/7	© CPC / EPO
CC	- C07D411/10
TI	- linked by a carbon chain containing aromatic rings

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- CPD 201509
- CPD 201510
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Van kérdés?

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