Universidade Federal do Rio de Janeiro

Princípios de Química Medicinal

Parte 3

30ª Semana Acadêmica de Farmácia da Faculdade de Farmãcia da UFBA

"Saúde, Educação e Interdisciplinaridade: Inserção no Mercado de Trabalho e Transformação da Sociedade"

13-17 de setembro de 2010

Salvador, BA

Eliezer J. Barreiro

Professor Titular

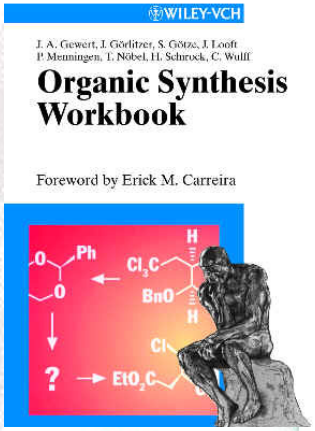
UFRJ

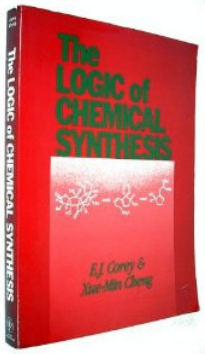
Conteúdo

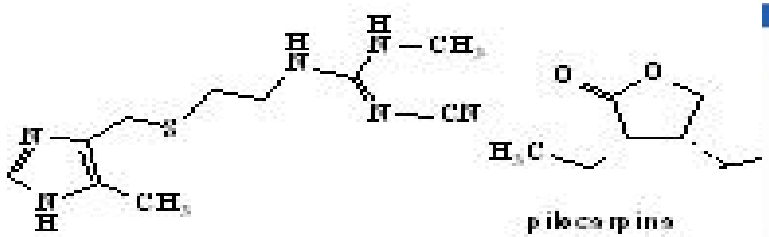
DEFINIÇÃO; os Pioneiros; Ernest forneau; Alfred Burger; a EVOLUÇÃO cronológica **DA** QUÍMICA Medicinal; os FÁRMACOS e o **Nobel**; Emil Fischer; Paul Ehrlich; Robert KOCH/louis Pasteur; *Alexander* Fleming; Ernest Chain; Howard FLOREY; George ***Hitchings;*** Gertrude Belle ELION; *Sir* James W. *Black*; bent *Samuelsson*; SUNE bergstron; John VANE; A. von Szent-Györgyi; W. N. Haworth; Linus C. Pauling; Arthur Kornberg; a **INTERDISCIPLINARIDADE**; as MOLÉCULAS dos *fármacos*; as *moléculas* PIONEIRAS; cronologia da DESCOBERTA de *fármacos*; os produtos NATURAIS e a *descoberta* de fármacos; a cadeia da *descoberta* dos FÁRMACOS; como nascem os FÁRMACOS; o PARADIGMA de Fischer; abordagem fisiológica;os BIORRECEPTORES; o modelo chave-fechadura; αbeto*S* *bioquímicos*; bioinformática & *QUÍMICA* COMPUTACIONAL; Topografia 3D dos BIORRECEPTORES; as CHAVES; TIPOS de interações FÁRMACOS-biorreceptores; SIMILARIDADE e dissimilaridade MOLECULAR; *reconhecimento* MOLECULAR; as *fases* DA ação dos FÁRMACOS; FASE farmacocinética; *metabolismo* dos fármacos; CYP450; RATO transgênico *humanizado*; *conceito* de grupamento FARMACOFÓRICOS, *auxofóricos*; *conceito* de COMPOSTO-protótipo; moléculas INTELIGENTES; fármacos sintéticos; *planejamento* RACIONAL; *Cimetidina;* **SILDENAFILA;** *lodenafila*; estatinas; ORLISTAT; novos fármacos; *rimonabanto*; ziconotídeo; considerações finais; *mercado* FARMACÊUTICO; MOLÉCULAS bilionárias; **LASSBio**; exemplos DE *casa*; COXIBES; *LASSBio-294 & 596*; *BIBLIOGRAFIA*; convite; agradecimentos.

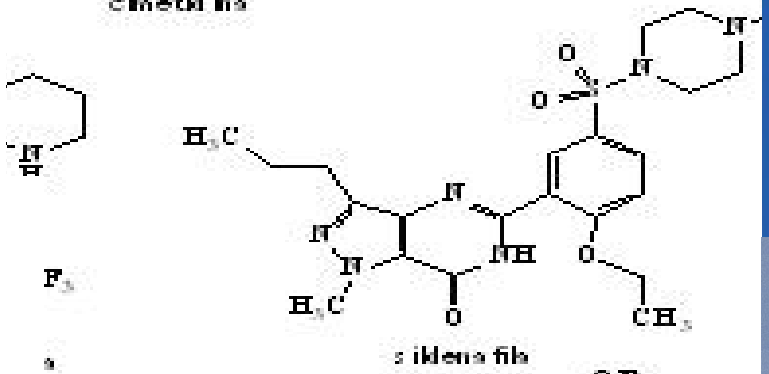
Moléculas inteligentes

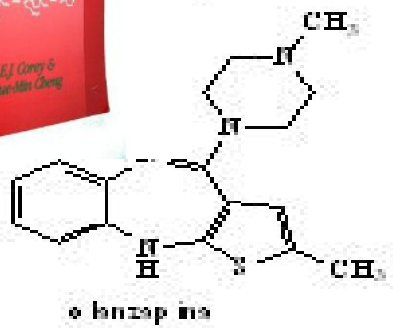
Química Medicinal

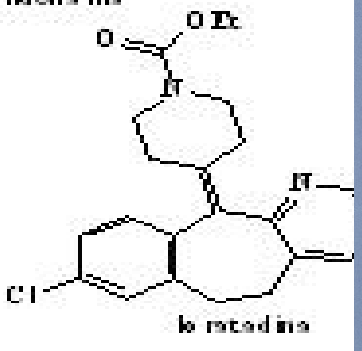


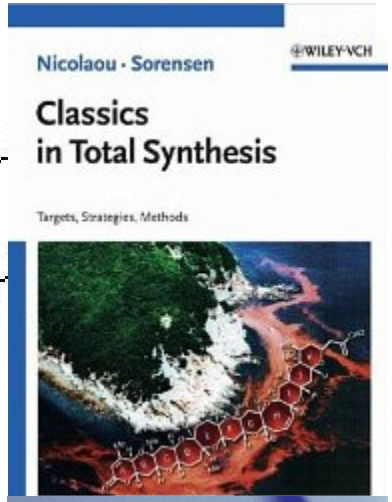


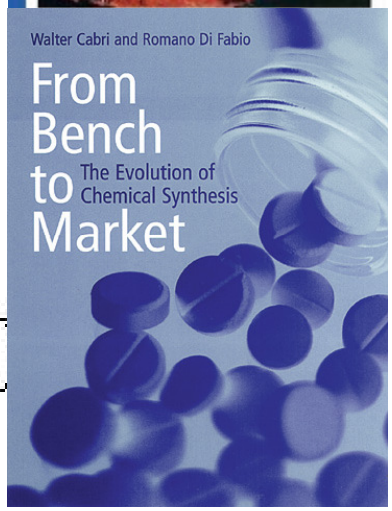


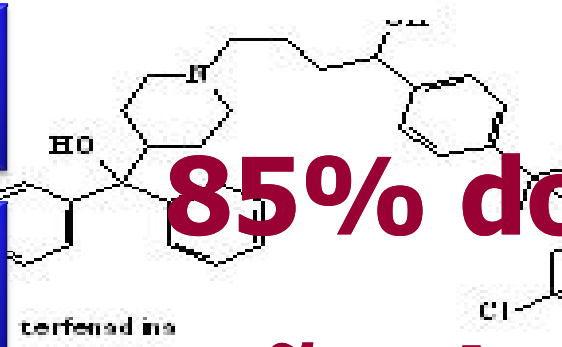


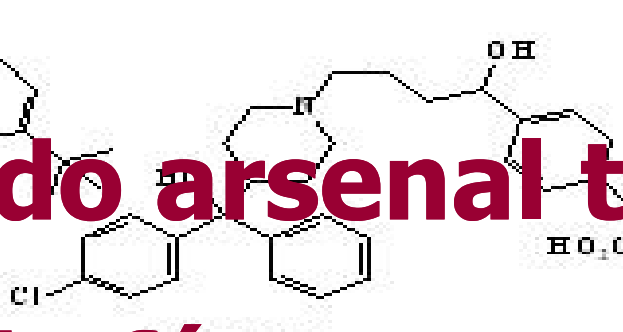


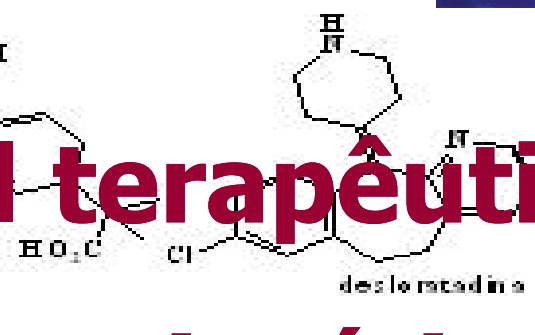












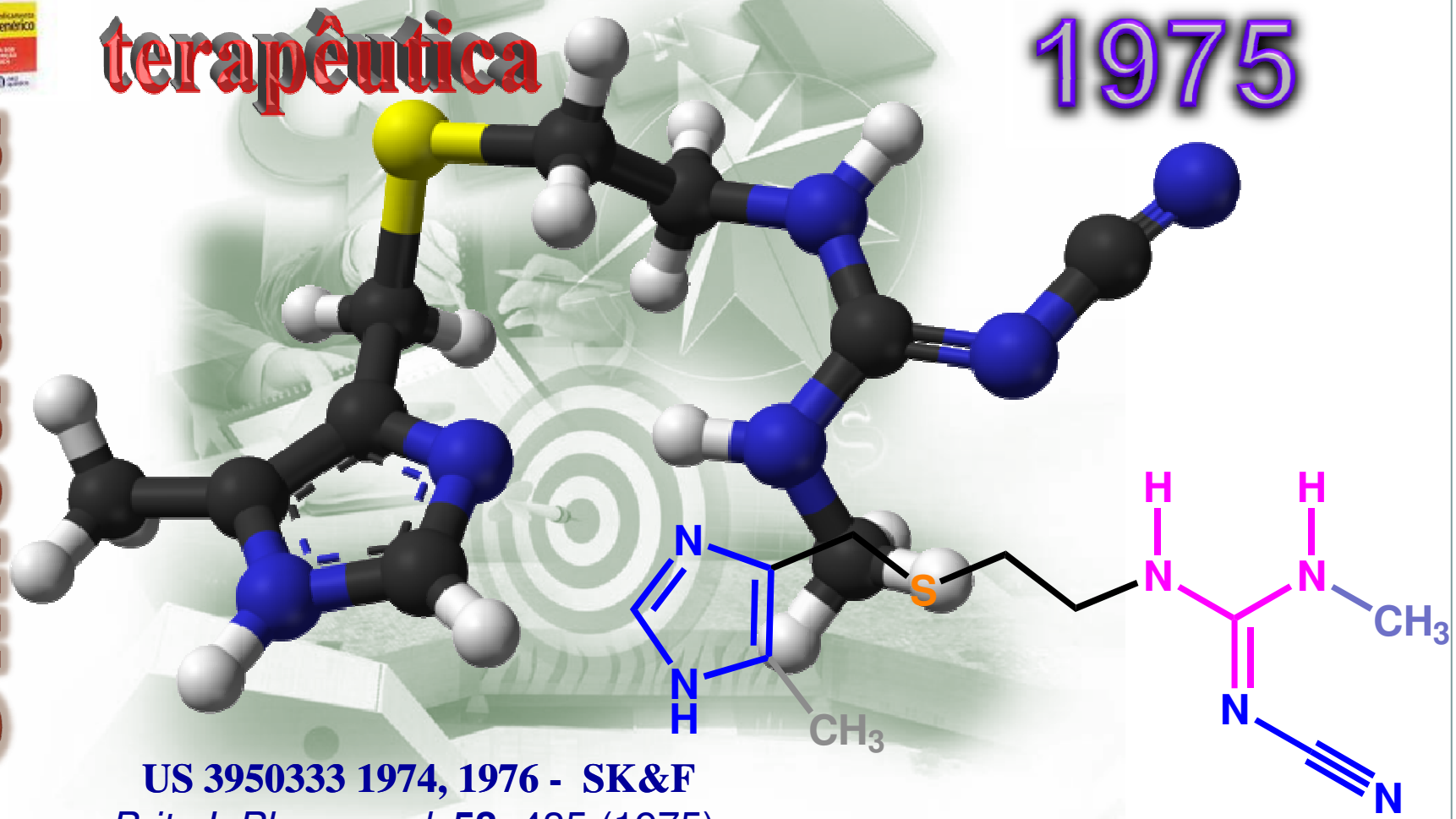
85% do arsenal terapêutico são de fármacos sintéticos

O desenvolvimento racional

Inovação terapêutica

1975

Cimetidina



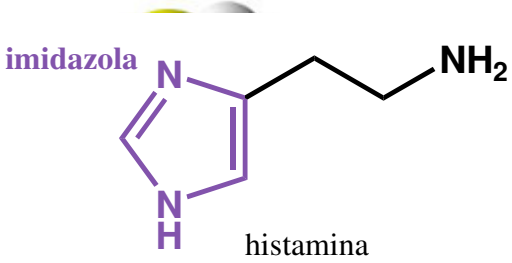
US 3950333 1974, 1976 - SK&F

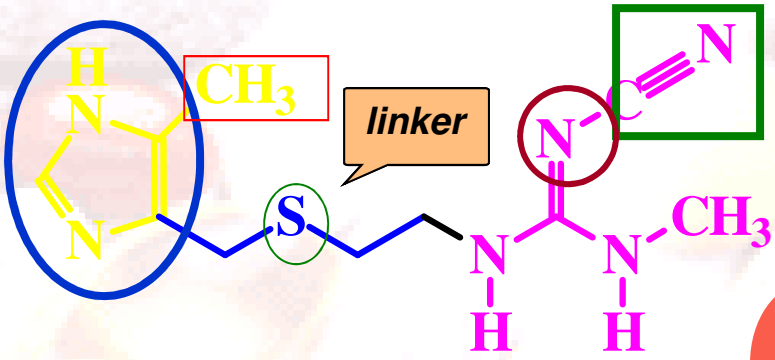
Brit. J. Pharmacol. **53,** 435 (1975).

James Black, Robin Ganellin, Emmett, Durant

$C_{10}H_{16}N_6S$

Uma invenção...





1975 - SK&F (Black, Ganellin, Emmet & Durant)

US 3950333 1974, 1976

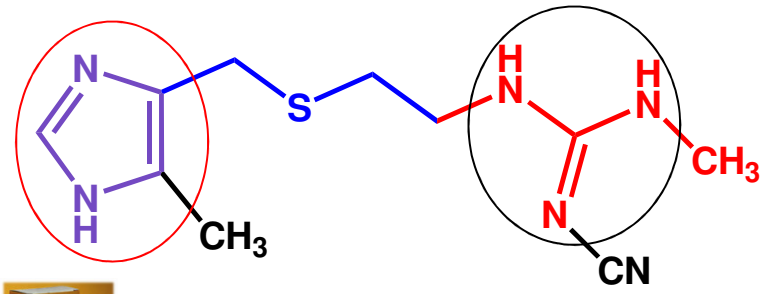
Brit. J. Pharmacol. 1975, **53,** 435

= inovação terapêutica !

Primeiro fármaco a atingir US$ 1 bilhão em vendas no ano do lançamento (1979)

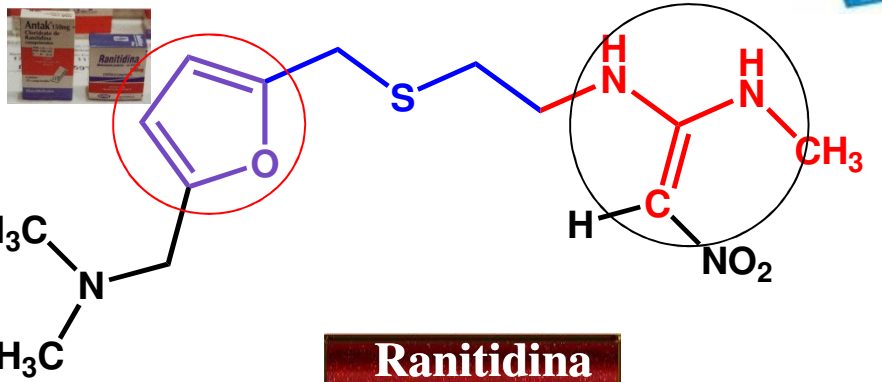
Os inventores: C. Robin Ganellin, Graham J. Durant, Michael E. Parsons, & James W. Black (Prêmio Nobel de Medicina em 1988) (foto →) + John C. Emmett, William A. M. Duncan, 1975;

JW Black, WAM Duncan, CJ Durant, CR Ganellin & EM Parsons, Definition and Antagonism of Histamine H_2-receptors, *Nature* 1972, *236*, 385-390 (doi:10.1038/236385a0)



Cimetidina

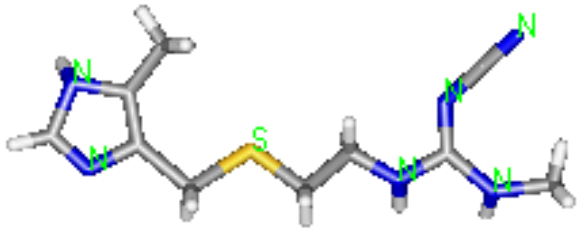
Robin Ganellin *et al.*, 1974
US 3950333 1974, 1976 - SK&F
Brit. J. Pharmacol. **53,** 435 (1975).

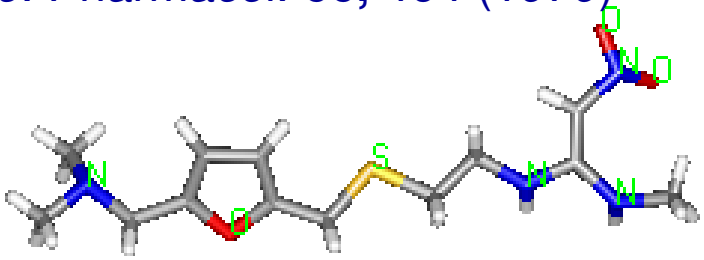


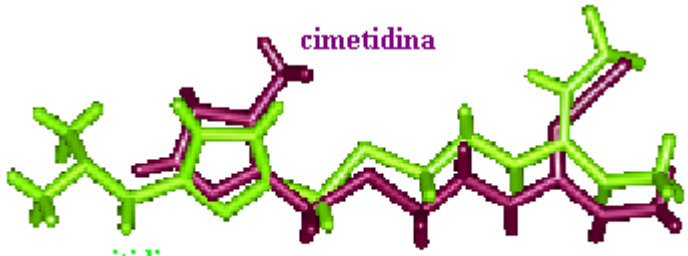
Ranitidina

Barry J. Price *et al.*, 1978
US 4128658 1978 - Allen & Hanburys
Brit. J. Pharmacol. **66,** 464 (1979)

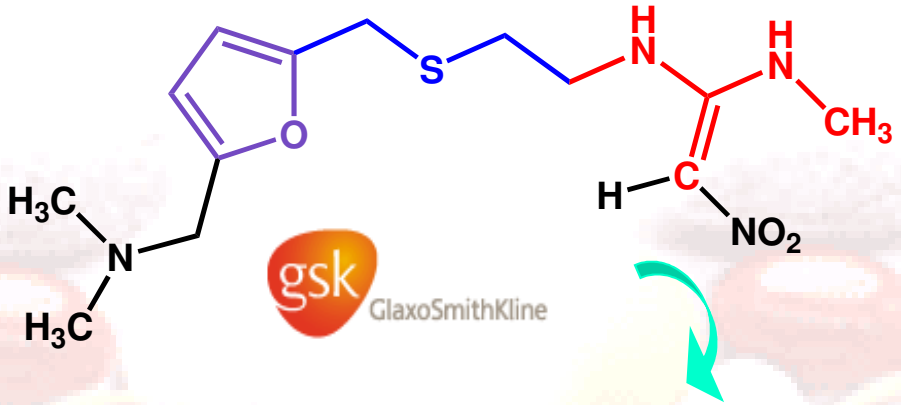
similaridade molecular







me-too



2008 annual results: **US$ 36,5 bi**

(~ > 10%/y)

***ca.* 21% do faturamento origina-se em NP's**

Investimentos RD&I: > US$ 2,04 bilhões

4 produtos com vendas > US$ 1 bi

80 fábricas em 37 países com 100.000 empregos

(*ca.* 16.500 em RD&I)

***Pipeline*: 51 projetos em fase pré-clínica**

158 projetos em desenvolvimento:

85 NCE's, 20 vacinas, 45 produtos

http://biopharm.gsk.com - Updated May 15, 2009

Top 15 Global corporations

	Empresa	Vendas (US$mi)	Sede
1	Pfizer	43,363	US
2	GlaxoSmithKline	36,506	UK
3	Novartis	36,506	Switzerland
4	Sanofi-Aventis	35,642	France
5	AstraZeneca	32,516	UK/Sweden
6	Hoffmann–La Roche	30,336	Switzerland
7	Johnson & Johnson	29,425	US
8	Merck & Co.	26,191	US
9	Abbott	19,466	US
10	Eli Lilly and Company	19,140	US
11	Amgen	15,794	US
12	Wyeth	15,682	US
13	Teva	15,274	Israel
14	Bayer	15,660	Germany
15	Takeda	13,819	Japan

IMS Health 2008

propranolol
1964

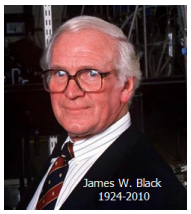
J. Black *et al.*, *Br. J. Pharmacol. Chmother.* **1965**, *25*, 577

α-naftol

pronetalol
1959

β-naftol

pilocarpina



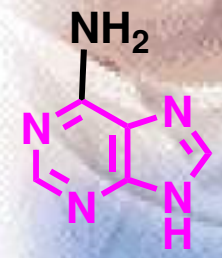
James W. Black, 1988 - "Pronethalol always seemed to us to be a prototype drug, good enough to answer questions of principle, but not good enough to be marketable"

adrenalina

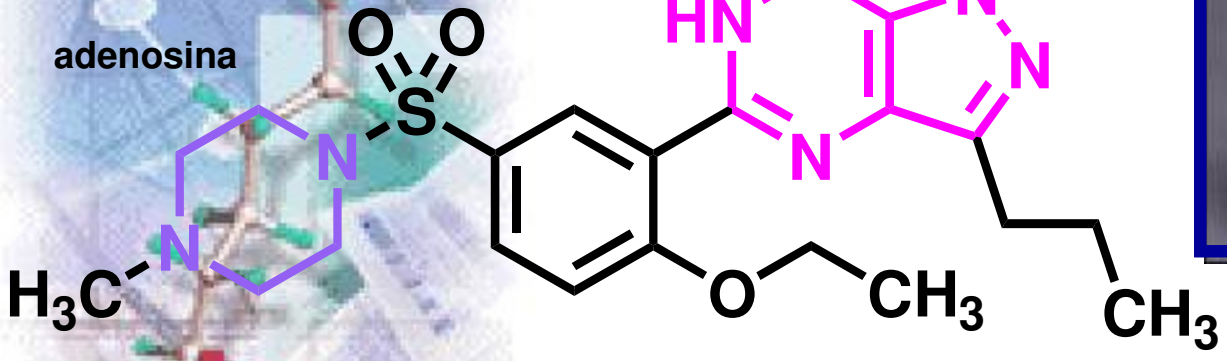
isoprenalina / isoproterenol

1958 - DCI
β-bloquedor

A descoberta do sildenafila



adenosina



sildenafila

Pfizer

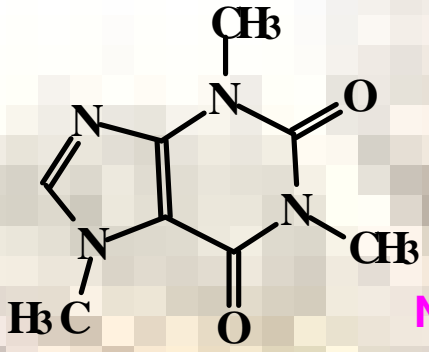
LASSBio®

Disfunção erétil

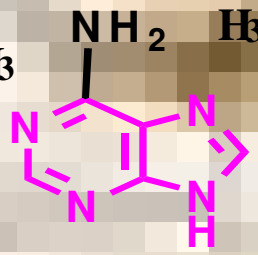
angina

PDE-i

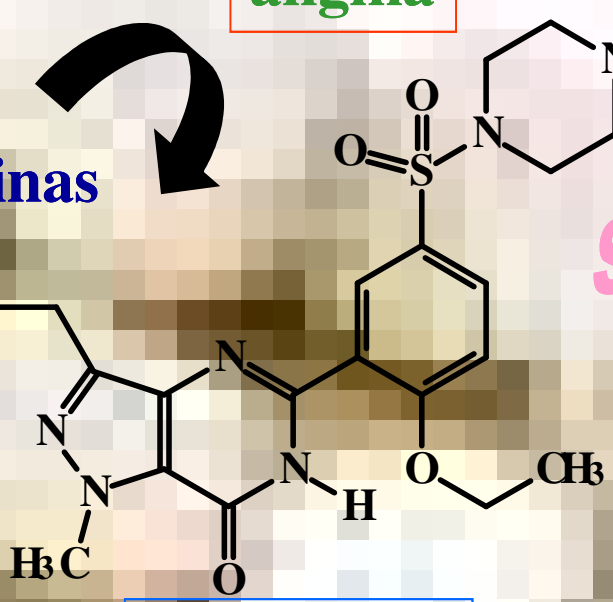
Metil-xantinas



Cafeína/teofilina

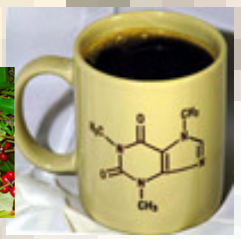


adenosina



sildenafila

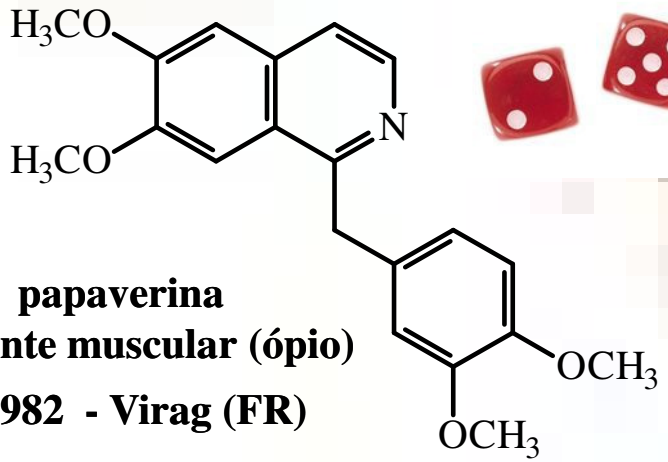
Simon Campbell



Fase 1

serendipidade

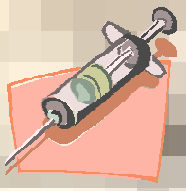
PDE-Vi



papaverina

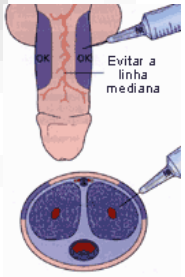
relaxante muscular (ópio)

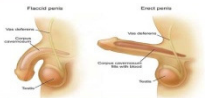
1982 - Virag (FR)



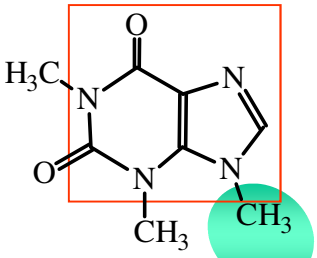
alprostadil injetável

Caverject^{R}

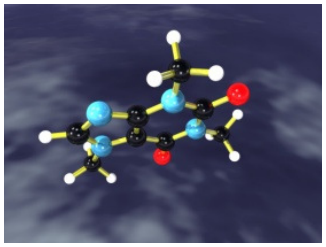




Disfunção erétil



teofilina



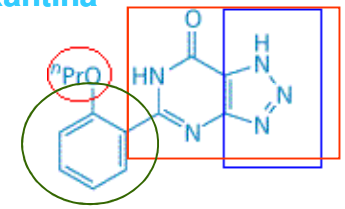
Corpus cavernosum

NO

Cell membrane

Guanylate cyclase

análogo xantina



Zaprinast

PDEi

GTP

GMP

bioisosterismo

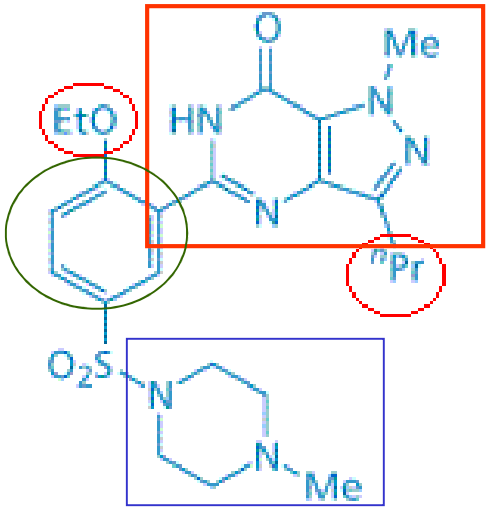
cGMP

Phosphodiesterase

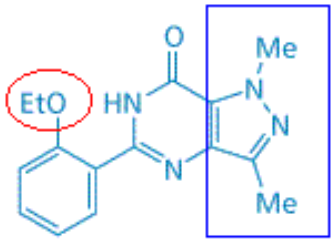
Erection

Smooth muscle relaxation

PDE-5 >> 6, 4



Sildenafil



Pirazolopirimidona

Viagra

NK Terret *et al.*, Bioorg. Med. Chem. Lett 1996, 6, 1819

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journal homepage: www.elsevier.com/locate/ejphar

Pharmacological characterization of a novel phosphodiesterase type 5 (PDE5) inhibitor lodenafil carbonate on human and rabbit corpus cavernosum

Haroldo A. Toque, Cleber E. Teixeira, Raquel Lorenzetti, Cristina E. Okuyama, Edson Antunes, Gilberto De Nucci *

Department of Pharmacology, Faculty of Medical Sciences, UNICAMP, Campinas, SP, 13081-970, Brazil

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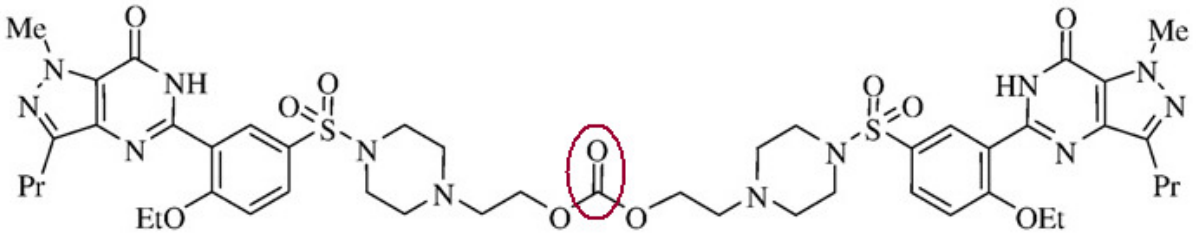
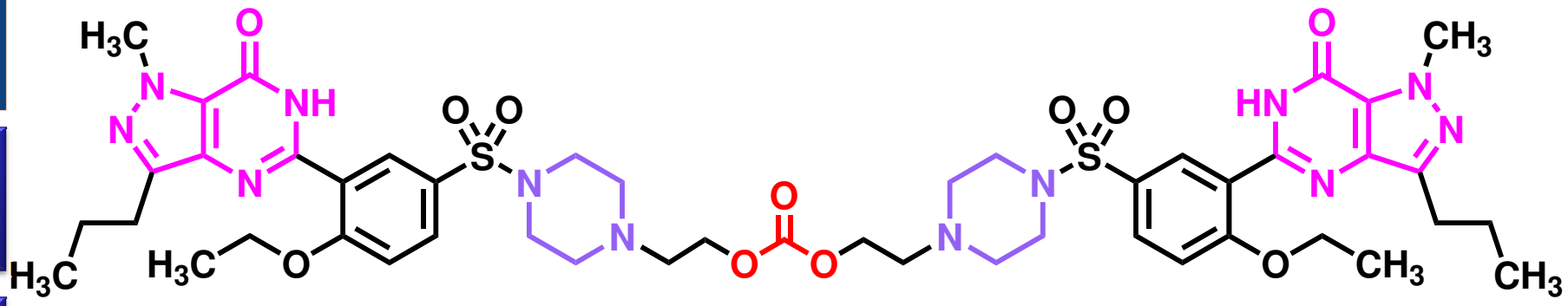
Sildenafil
Nitric oxide
Cyclic GMP
Pro-drug
Dimerization

ABSTRACT

Nitrergic nerves and endothelial cells release nitric oxide (NO) in the corpus cavernosum, a key mediator that stimulates soluble guanylyl cyclase to increase cGMP levels causing penile erection. Phosphodiesterase 5 (PDE5) inhibitors, such as sildenafil, prolong the NO effects by inhibiting cGMP breakdown. Here, we report a novel PDE5 inhibitor, lodenafil carbonate, (Bis-(2-[4-[4-ethoxy-3-(1-methyl-7-oxo-3-propyl-6,7-dihydro-1*H*-pyrazolo[4,3-*d*]pyrimidin-5-yl)-benzenesulfonyl]piperazin-1-yl}-ethyl)carbonate) that is a dimer of lodenafil. We therefore aimed to compare the effects of sildenafil, lodenafil and lodenafil carbonate on in vitro human and rabbit cavernosal relaxations, activity of crude PDE extracts from human platelets, as well as stability and metabolic studies in rat, dog and human plasma. Pharmacokinetic evaluations after intravenous and oral administration were performed in male beagles. Functional experiments were conducted using organ bath techniques. Pharmacokinetics was studied in beagles by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), following oral or intravascular administration. All PDE5 inhibitors tested concentration-dependently relaxed (0.001–100 μM) phenylephrine-precontracted rabbit and human corpus cavernosum. The cavernosal relaxations evoked by either acetylcholine (0.01–100 μM) or electrical field stimulation (EFS, 1–20 Hz) were markedly potentiated by sildenafil, lodenafil and lodenafil carbonate. Lodenafil carbonate was more potent to inhibit the cGMP hydrolysis in PDE extracts compared with lodenafil and sildenafil. Following intravascular and single oral administration of lodenafil carbonate, only lodenafil and norlodenafil were detected in vivo. These results indicate that lodenafil carbonate works as a prodrug, being lodenafil the active moiety of lodenafil carbonate.

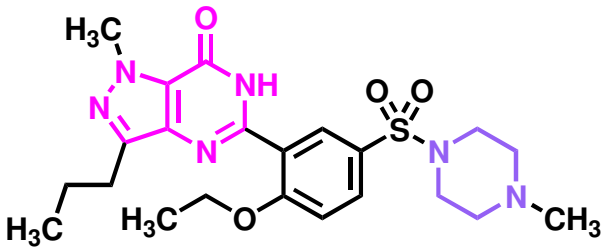


Lodenafil carbonate

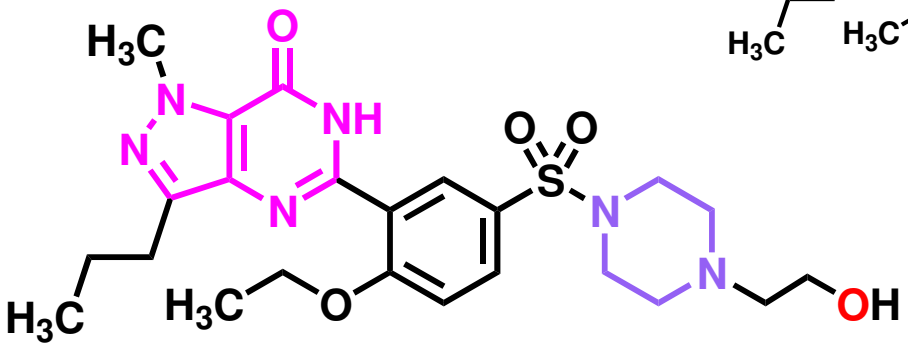


carbonato de lodenafila

in vivo



sildenafila



lodenafila

HA Toque, CE Teixeira, R Lorenzetti, CE Okuyama, E Antunes, G De Nucci, "Pharmacological characterization of a novel phosphodiesterase type 5 (PDE5) inhibitor lodenafil carbonate on human and rabbit corpus cavernosum", *European Journal of Pharmacology* **2008,** *591*, 189–95.

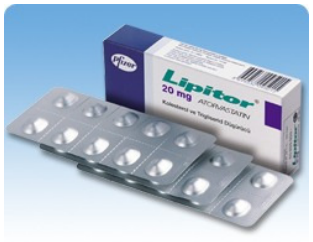
A descoberta das estatinas

Química Medicinal

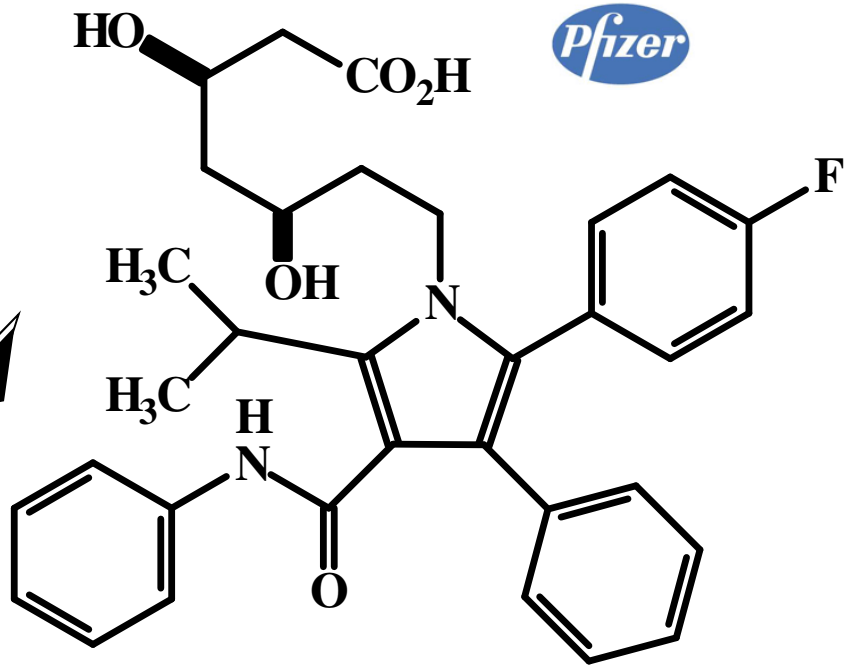
Estatinas: do protótipo natural ao super-fármaco

LDL = LIPOPROTEÍNA DE BAIXA DENSIDADE, COLESTEROL RUIM

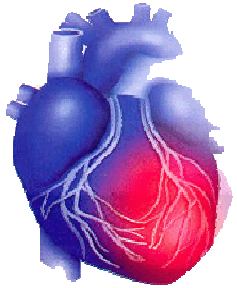
mevastatina



Pfizer

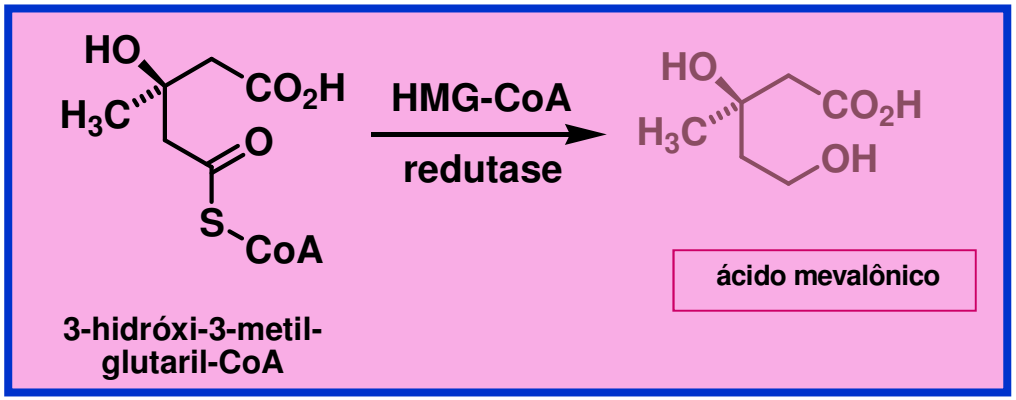


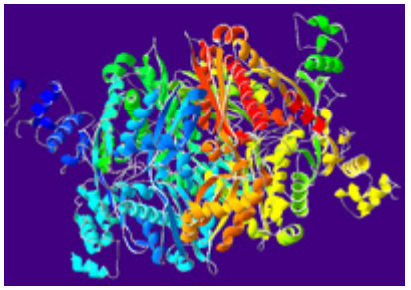
atorvastatina

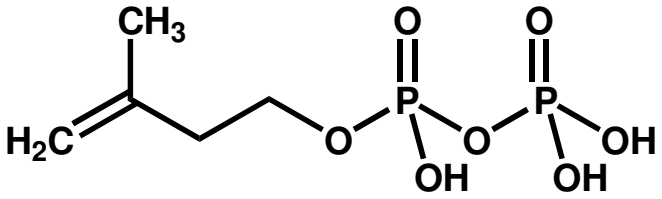


2009: US$ > 13,5 bi

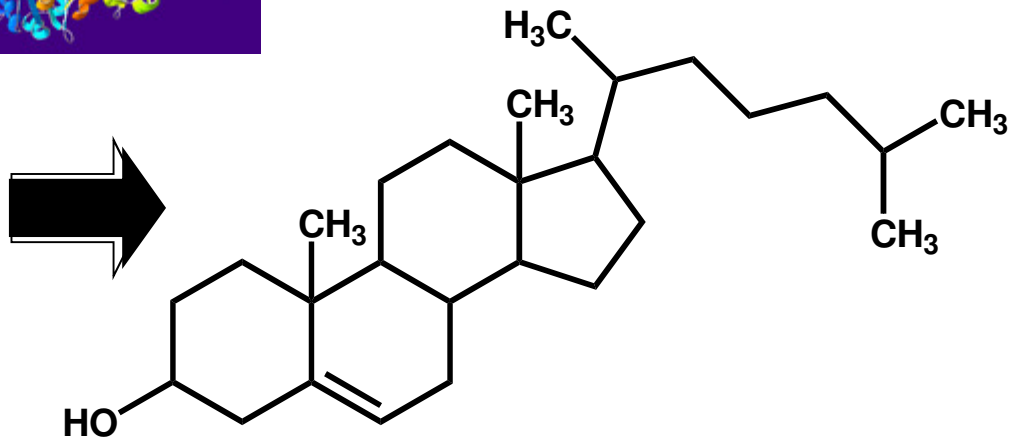
Biossíntese do colesterol







pirofosfato de isopentenila



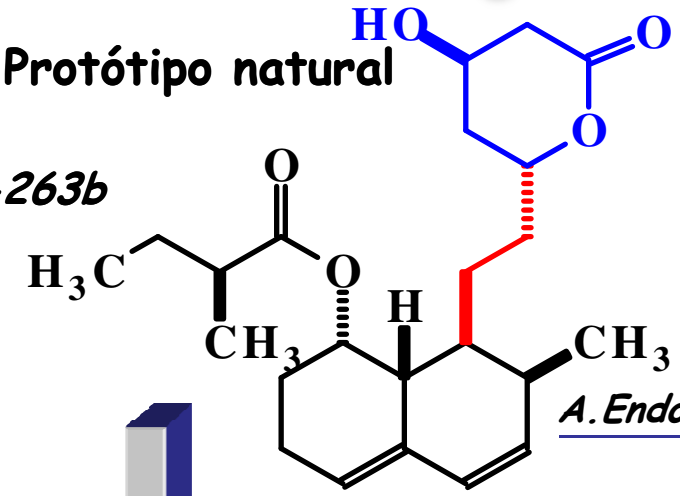
colesterol

Metabólito de Fungo

Akira Endo, Sankyo Co

1975 - Mevastatina (ML-263b

Protótipo natural



A.Endo, J. Antibiot. 1976, 29, 1346
Penicillium citrinum
Idem, Ibid, 1979,32,852
Monascus ruber
(compactina)

A.Endo, J. Med. Chem. 1985, 28, 01

Similaridade molecular

Arthur A. Patchett

J.Med.Chem. 2002,45, 5609.

γ-lactona

Mevilonina

Lovastatin (MK-803)
1980 - Merck & Co.
Aspergillus terreus

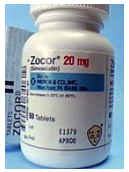
1987 - MS&D (Mevacor^{R})

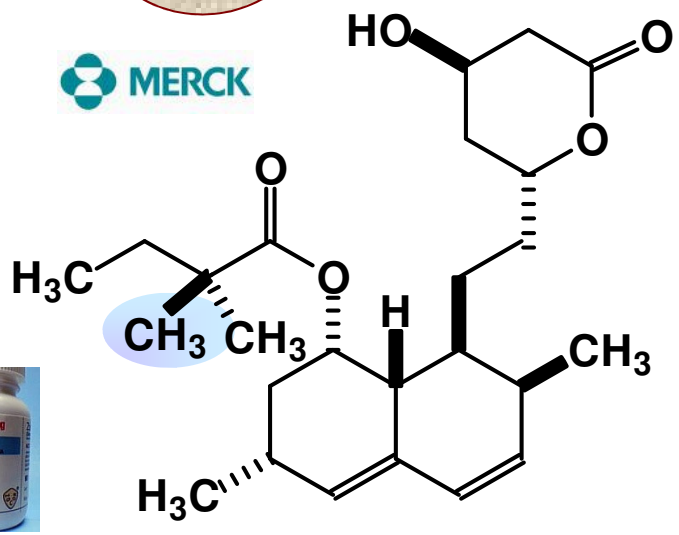
US$ 5,5 bi (2007)

Pró-fármaco

MERCK

*Sim*vastatin
(Zocor^{R})
MK-733
1988

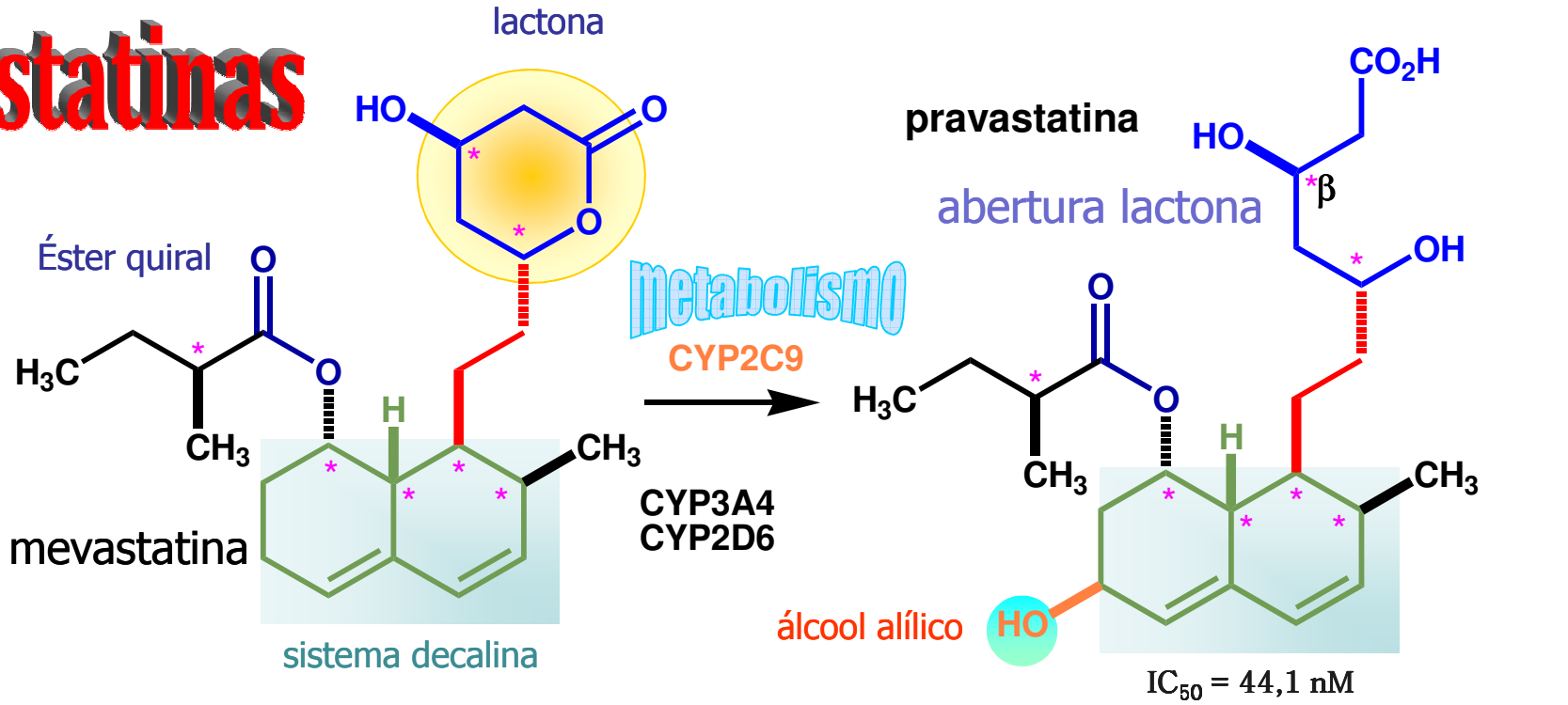


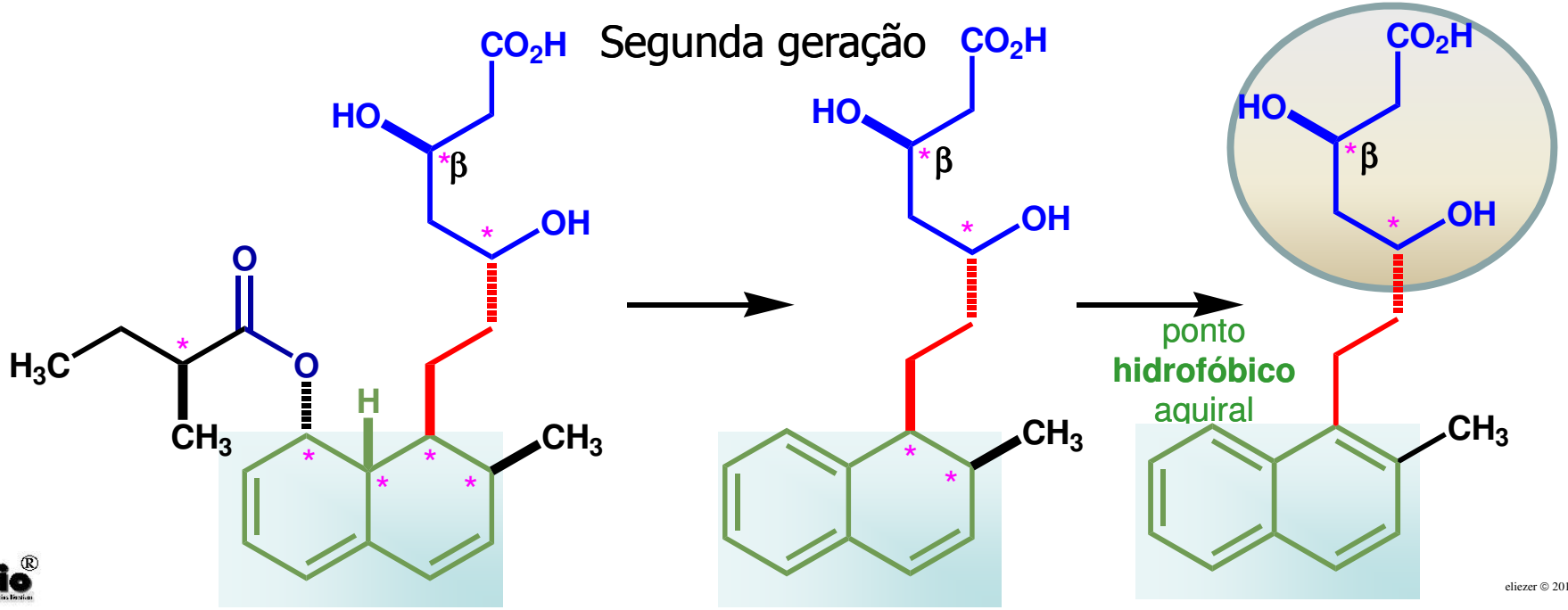


J. Med. Chem. 1986, *29*, 849

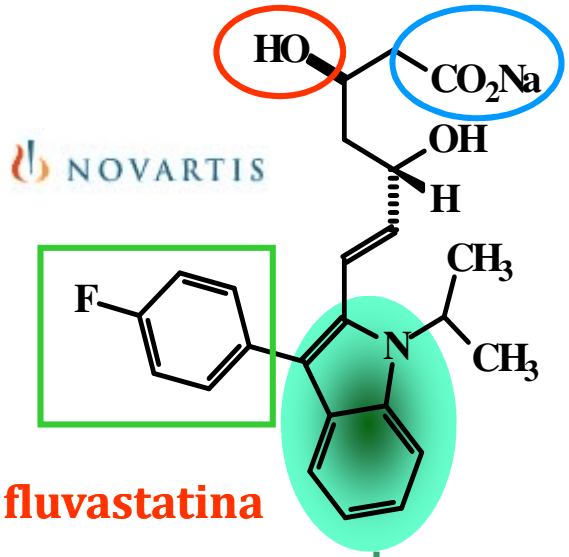
IC_{50} = 11,2 nM

Estatinas





Gênese das estatinas de segunda geração (sm)

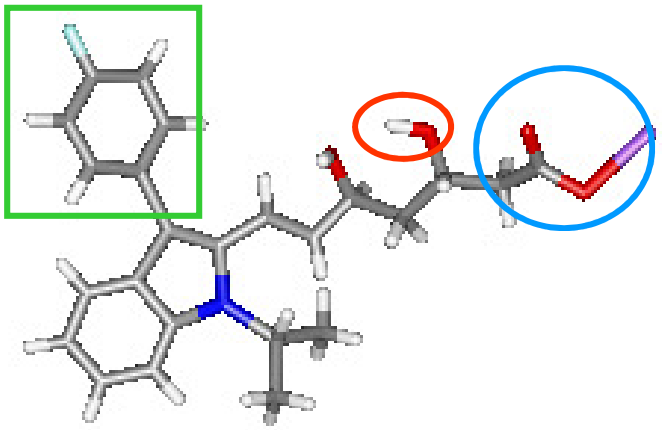


NOVARTIS

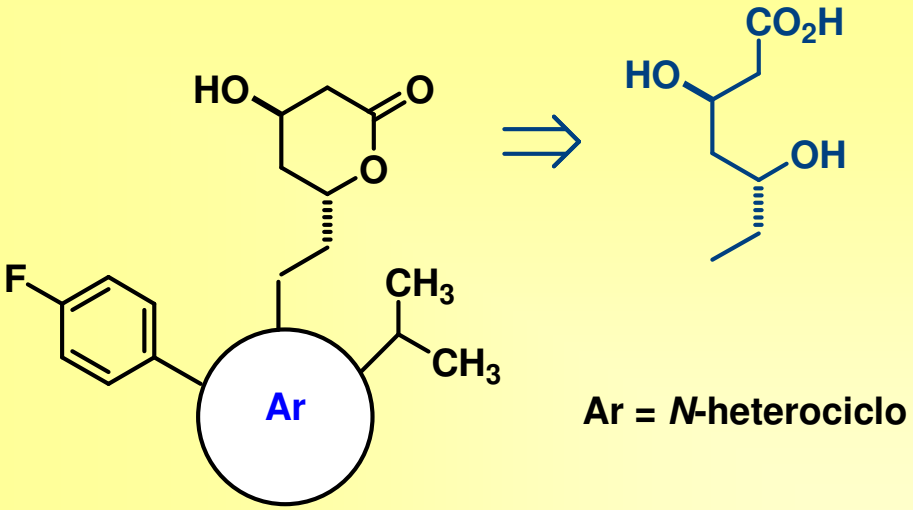
fluvastatina

IC_{50} = 27,6 nM

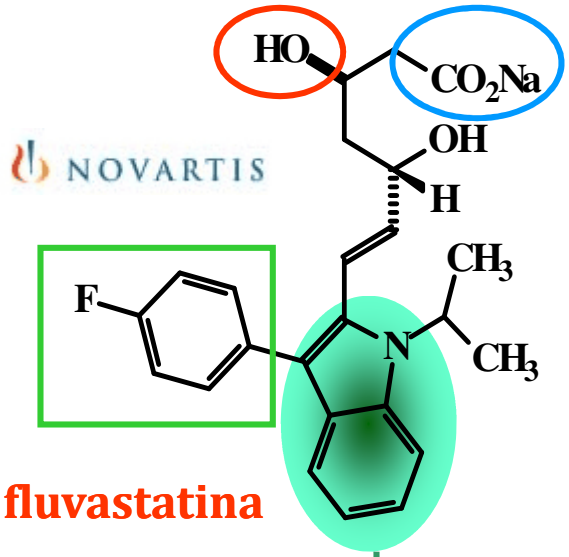
Sub-unidade hidrofóbica = aromática



Qumiotipo das estatinas



Gênese das estatinas de segunda geração (sm)

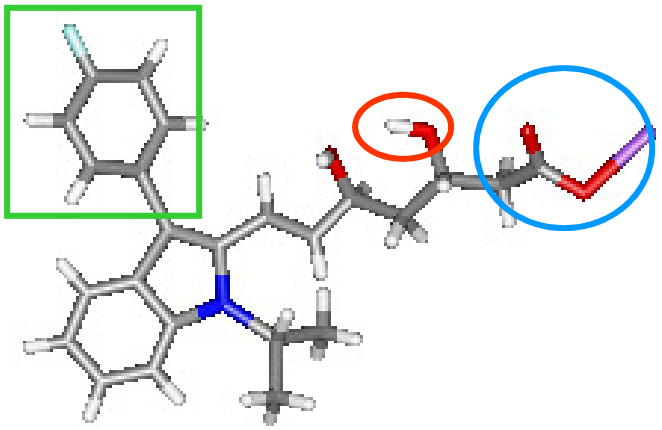


NOVARTIS

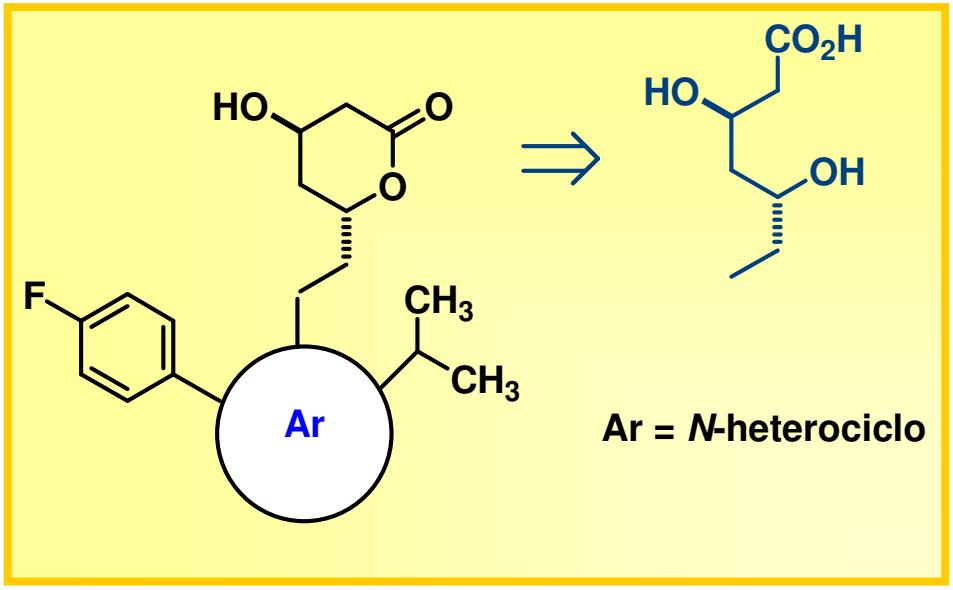
fluvastatina

IC_{50} = 27,6 nM

Sub-unidade hidrofóbica (aromática)

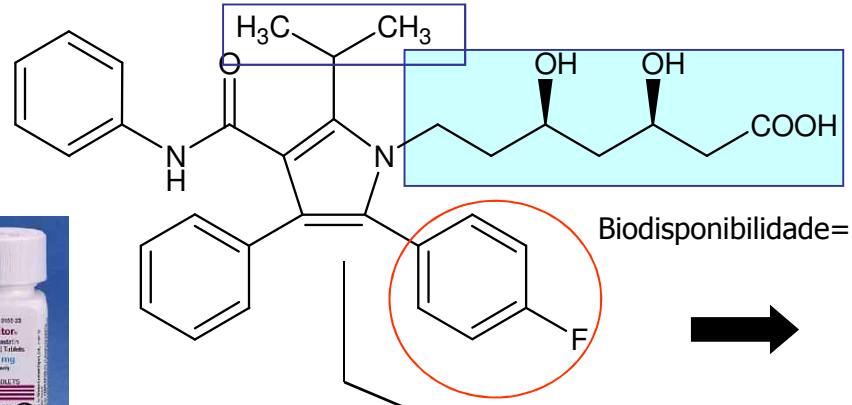


Qumiotipo das estatinas

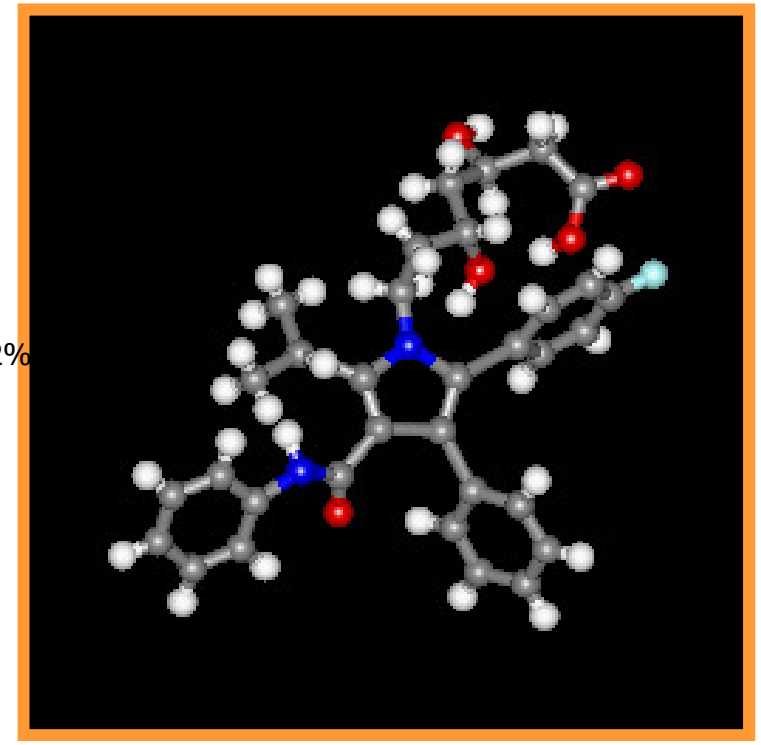


Estatinas

ácido (*N*-pirrol)-3,5-di-hidróxi-heptanóico



Biodisponibilidade=12%

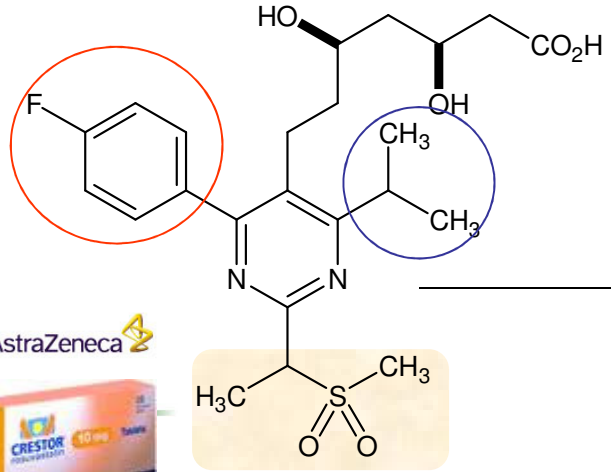


Pfizer

atorvastatina

IC_{50} = 8,2 nM

Ar

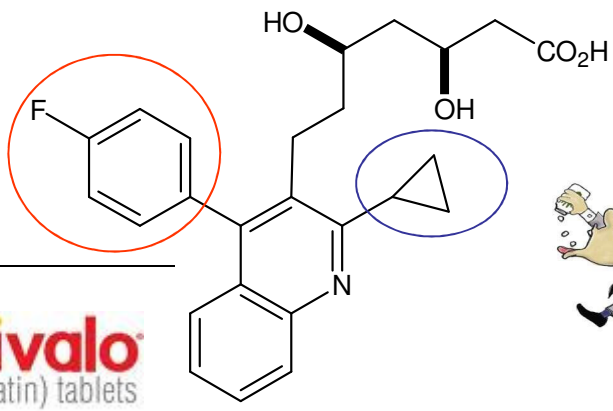


AstraZeneca

isponibilidade = 20%

rosuvastatina

IC_{50} = 5,4 nM



Livalo (pitavastatin) tablets

Kowa Pharmaceuticals

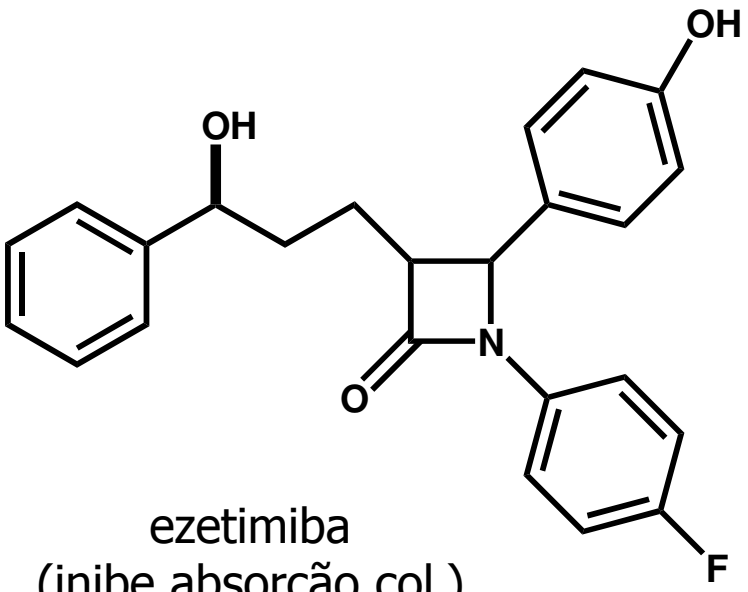
Biodisponibilidade=60%

pitavastatina

IC_{50} = 3,4 nM

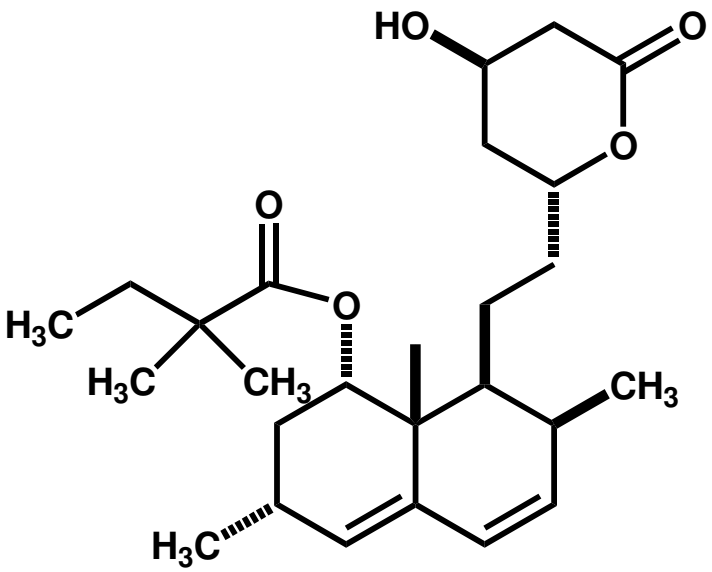
LASSBio®

Schering-Plough



ezetimiba
(inibe absorção col.)

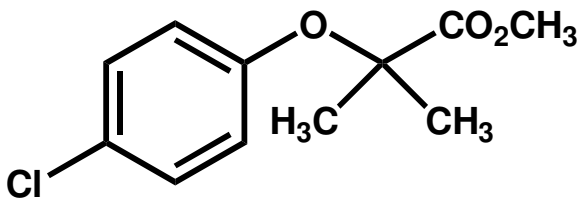
MERCK
Be well



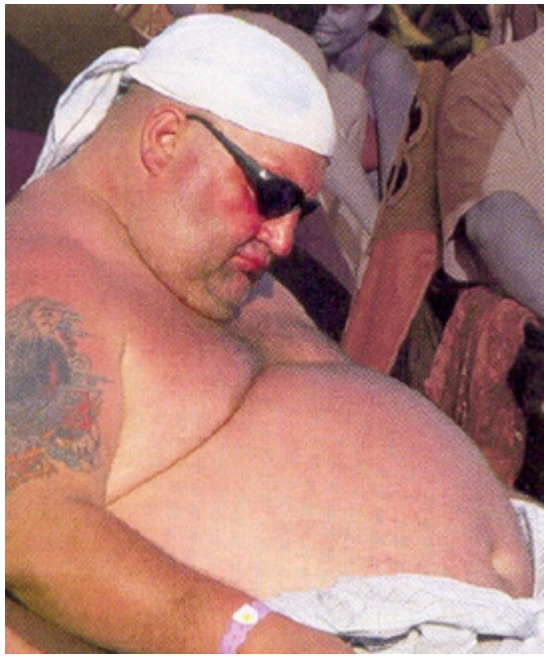
Simvastatina
(HMGCoARi)

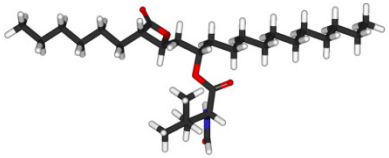
VYTORIN
(ezetimibe/simvastatin) tablets

American Academy of Cardiology's
57th Annual Scientific Session (2008)
Dislepidemia = hipercolesterolemia, LDL &
hipertrigliceridemia

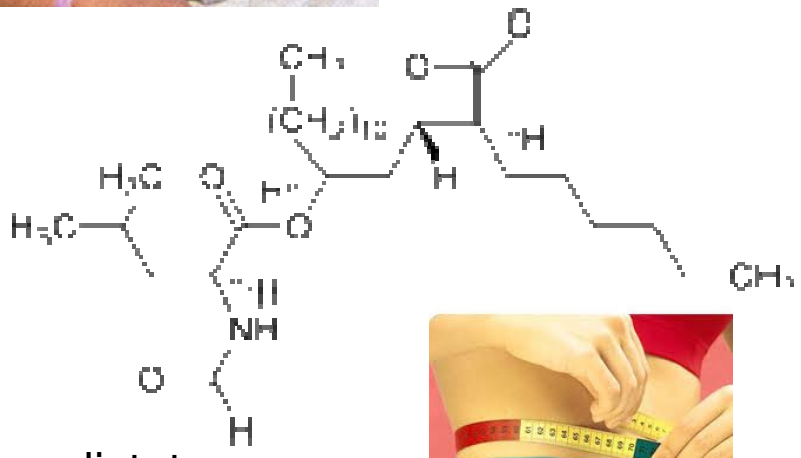


Inovação terapêutica: obesidade





Animal transgênico com obesidade provocada, representou primeiro modelo in vivo para estudo de novos fármacos anti-obsidade.



orlistat

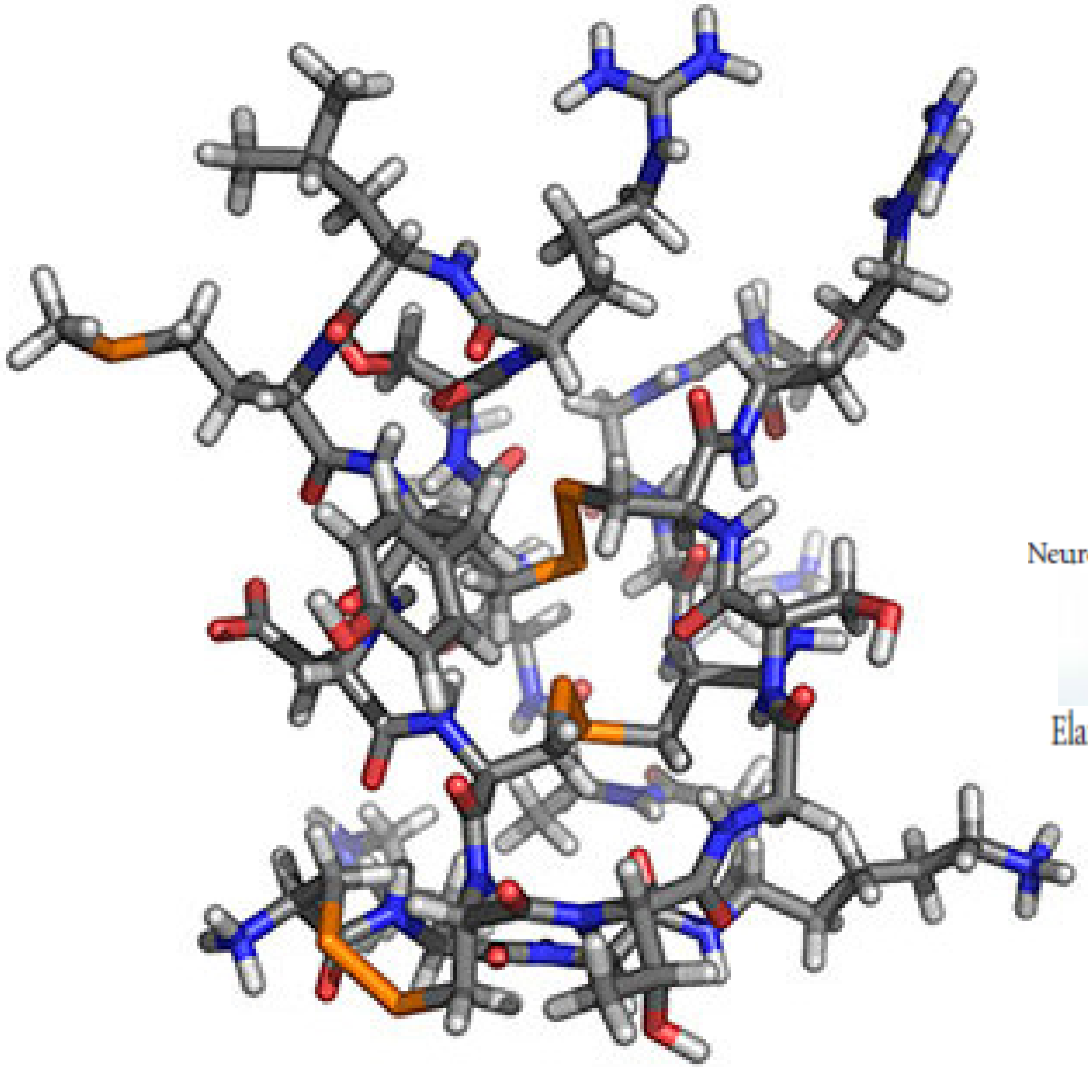
1980 - Michael McIntosh & Baldomero Olivera

Ziconotídeo

$C_{102}\ H_{172}\ N_{36}\ O_{32}\ S_7$

FDA em 28/12/2004; Eur Comm. em 22/02/2005

Uso intratecal



25 aa

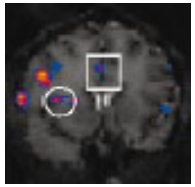
Conus magus

SNX-111

Neurex (Menlo Park, CA)

Elan Pharmaceuticals

(Dublin, Ireland



Antagonista de canais Ca^{++} voltagem dependentes tipo-N

Considerações finais

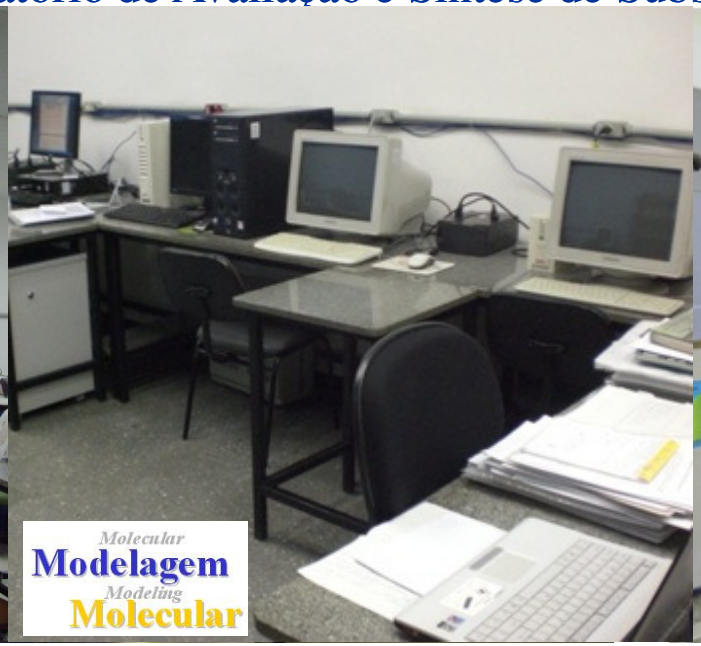
Química Medicinal

LASSBio

Laboratório de Avaliação e Síntese de Substâncias Bioativas

19/04/1994

Laboratório de Avaliação e Síntese de Substâncias Bioativas

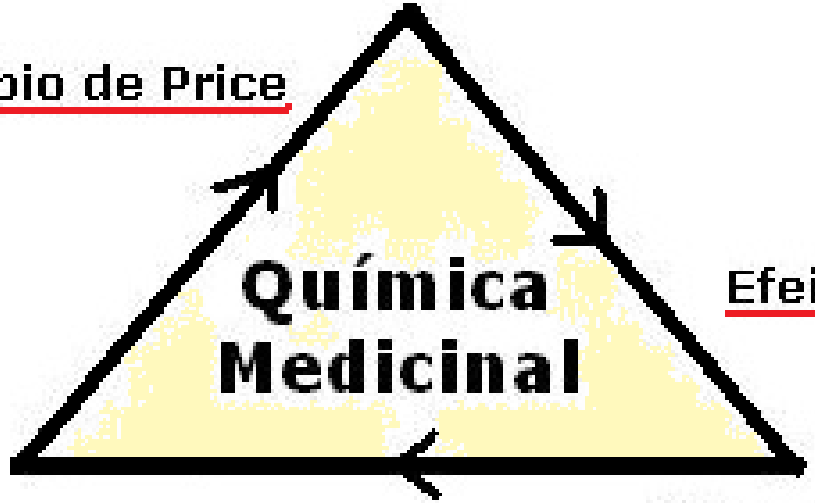


LASSBio

Abordagem Fisiológica

Síntese orgânica medicinal

Princípio de Price



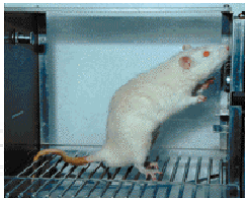
Efeito porta-ao-lado

Química computacional

modelagem molecular

Bioensaios

in vivo / in vitro



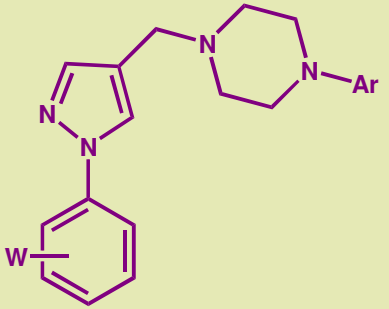
Universidade Federal do Rio de Janeiro

Novos Compostos-Protótipos Descobertos no LASSBio®

LASSBio-294

USPTO Patent # 7.091.238
August 15, 2006
2nd license agreement
ORD, UM Maryland, Baltimore, USA

LASSBio-579



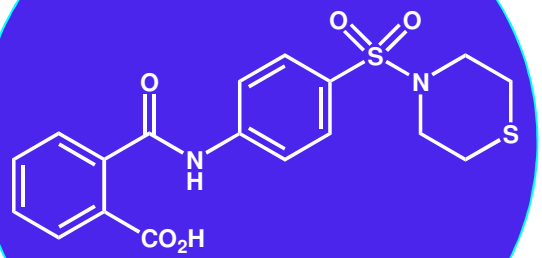
INPI # 0303465-8 de 05/09/2003

LASSBio-585

Thienylhydrazon with digitalis-like properties (positive inotropic effects)
August 15, 2006
Publication Number: 07091238

LASSBio-581

LASSBio-596



Sob contrato c/ empresa farmacêutica nacional

Otimização do protótipo

Otimização do protótipo *Otimização do protótipo*

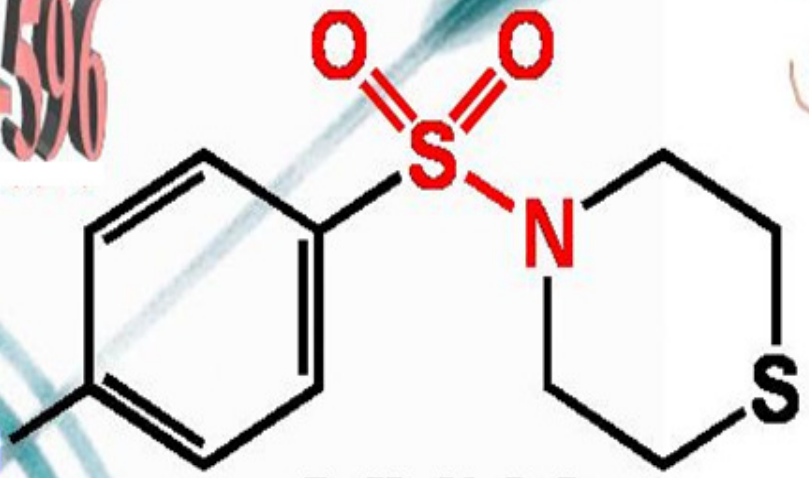
LASSBio®

Universidade Federal do Rio de Janeiro

New lead-compound for asthma

LASSBio-596

2010



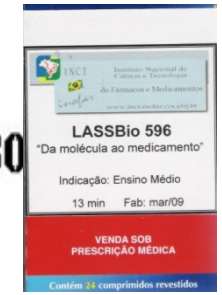
$C_{18}H_{18}N_2O_5S_2$

406,4

Log P = 2 / CLogP = 1,80

MR = 103,02

Pre-clinic studies



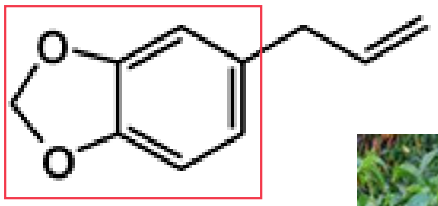
PIBR 0208767-7 - 08/11/2002
PIBR 0401660-2 - 27/04/2004

COPD

M. Lima *et al.*, *Bioorg. Med. Chem. Lett.*, **12**, 1533, 3067 (2002) ; P. R. M. Rocco *et al.*, *Eur. Respir. J.*, **22**, 20 (2003) ; M. Lima *et al.*, A*ntii-nflammatory & Anti-allergy Agents in Medicinal Chemistry*, **3**, 9 (2004) ; J. V. Bevilaqua *et al.*, *Biochem. Biotechnol.*, **121**, 117 (2005); M. S. Alexandre-Moreira *et al.*, *International Immunopharmacology*, **5**, 485 H. S. Campos *et al.*, *Braz. J. Med. Biol. Res.*, **39**, 283 (2006) ; L.M. Lima *et al.*, *Anti-inflammatory & Anti-alergy n Medicinal Chemistry*, **5**, 79 (2006)

Novo protótipo de fármaco cardioativo: LASSBio-294

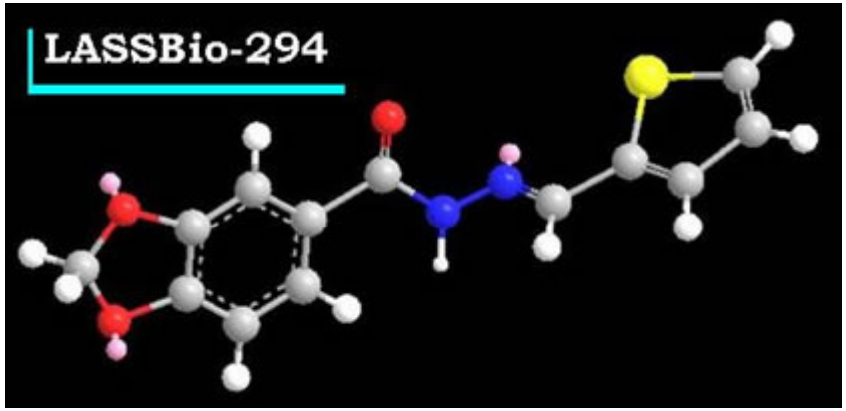
Matéria-prima abundante & sustentável



Safrol

Anel benzodioxola

Bióforo natural



Fórmula molecular $C_{10}H_{10}O_2$

Pêso molecular 162.19

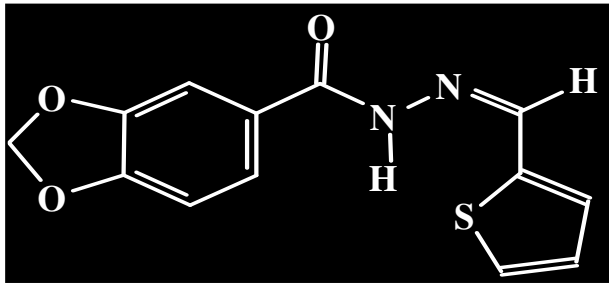
Densidade 1.096 g/cm3

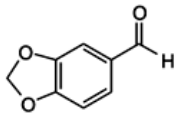
P.F. 11 °C

P.E. 232-234 °C

CAS # 94-59-7

IUPAC: 5-(2-Propenil)-1,3-benzodioxola





Piperonal

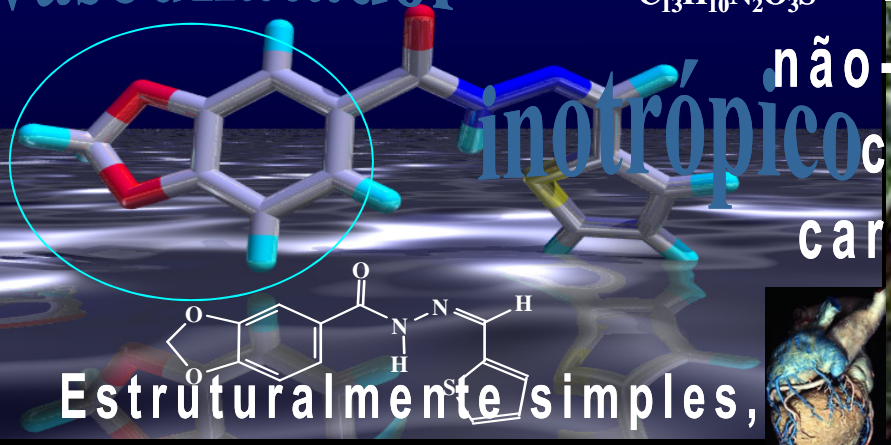
Novo Protótipo de Fármaco Cardioativo

LASSBio-294

vasodilatador

inotrópico

$C_{13}H_{10}N_2O_3S$



Estruturalmente simples, sinteticamente acessível em ótimos rendimentos, através de metodologia clássica, escalonada (1,0 M), a partir de produto natural abundante, acessível.

Safrol

Novo agente cardioativo, não-digitálico, não-adrenérgico, com potentes propriedades cardioativas & neuroprotetoras; Ativo por via oral; Sem toxicidade aguda, cito- ou genotoxicidade.

Piper longa

NAH

Patente

LASSBio

Laboratório de Avaliação e Síntese de Substâncias Bioativas

"Thienylhydrazon with digitalis-like properties (positive inotropic effects)" - Patente 07091238 (USPTO), 15 de agôsto de 2006; WO 2000-078754 (65 países) .

LASSBio®

Estudos de Toxicidade Aguda e Sub-aguda

✓**A toxicidade sistêmica aguda e sub-aguda foi investigada em ratos, por duas vias de administração, *p.o.* e *i.p.*, nas doses de 1000 μM/kg e 73 μM/kg, respectivamente (*i.p.*, administrando-se 2 vezes ao dia, durante 15 dias seguidos: ~ 100 vezes superior à ED_{50} *in vivo*).**

LASSBio-294

Novo protótipo de fármaco cardioativo

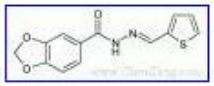
Não tem efeito letal, não provoca letargia, não reduz a motilidade, nem altera o pêso dos animais.

Não provoca alterações na contagem de células sanguíneas, hematócrito, nem altera a taxa de glicose, uréia, TGO, TGP, creatinina.

Não altera histopatologicamente orgãos vitais, tais como fígado, pulmão, SNC.

Não se observaram efeitos neurotóxicos em culturas de neurônios hipocampais de ratos, tratadas com LASSBio-294 (500 μM).
Efeito neuroprotetor foi observado em < doses.

Google lassbio-294 Pesquisar imagens Voltar aos resultados de imagens



Ver imagem em tamanho grande

242 x 92 - 2k - gif - www.chemdrug.com/.../SYNTHESIS/STR/31/311236.gif

A imagem pode ter direitos autorais.

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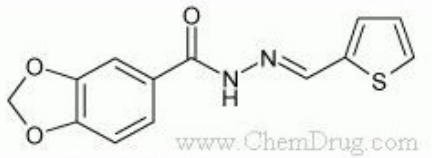
您现在的位置： >> 专业资料首页 >> 药物合成数据库 >> L-294, LASSBio-294,314021-07-3,C13-H10-N2-O3-S,(E)-N'-(Thien--药物合成数据库

【药物名称】 L-294, LASSBio-294

【化学名】 (E)-N'-(Thien-2-ylmethylene)-1,3-benzodioxole-5-carbohydrazide

【CAS登记号】 314021-07-3

【结构式】



【分子式】 C13-H10-N2-O3-S

【分子量】 274.299

【原研厂家】 LASSBio (Originator), University of Maryland (Originator)

【作用类别】 CARDIOVASCULAR DRUGS, Cerebrovascular Diseases, Treatment of, Heart Failure Therapy, NEUROLOGIC DRUGS, Positive Inotropic]ents, Phosphodiesterase III Inhibitors

AD-8717,181821-99-8,N-(2,6 DMP-802,,3-[2-[3-(4-Amidino]

Zonampanel, YM-872,21024 SB-221284,196965-14-7,5-(

推荐专业资料

ZINC00145813,ST5197865,	Oprea1_826548,MLS000122
ZINC00151021	IUPAC Name: 3-(2-chlorophe
ZINC00257502	MLS000716050,BAS 078671
STK138182,ZINC00302421,	IUPAC Name: (3E)-3-[(4-etho
Oprea1_091018,ST031273,	ZINC00104509
ZINC00084075	IUPAC Name: (2R)-1-(4-meth
IUPAC Name: (1R,,6R)-6-[(2-	Oprea1_406105
IUPAC Name: 6-hydroxy-1-(2-	ZINC00081150
STOCK2S-20570,ZINC0026	ZINC00214910
ZINC00230690	Oprea1_042214,CBDivE_01

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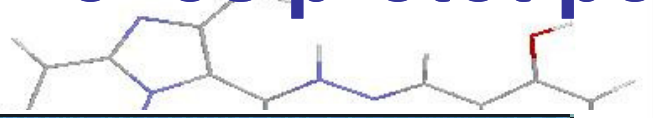
Banco de dados de moléculas =

Novos protótipos



Medichem Database:
Chemical, Biological and Pharmacological Applications

Molecular Form:	C16H14N4O2
IUPAC Nomenclature :	????????????
Fantasy Name :	Te te
Number of Quiral Centers :	0
Number of H-Bond Donors	
Number of H-Bond Acceptors	
Number of Free Bonds	4
Log P	2.0
Fusion Point	100
Functional Group:	Acylhydrazone

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A quimioteca do LASSBio tem 1565 compostos originais e ativos

Jmol

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Rotacionar

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Revista Virtual de Química
www.uff.br/rvq
Volume 1, Número 1, Janeiro-Março 2009

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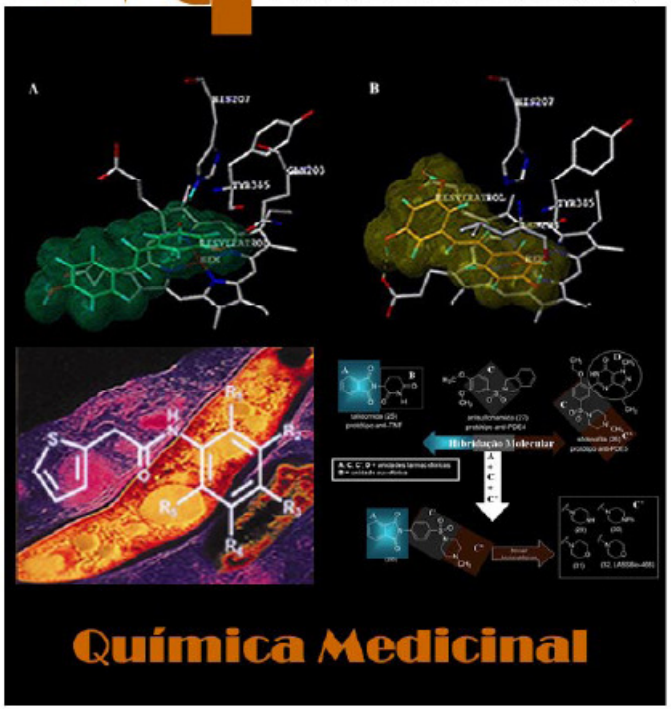

O medicamento é instrumento essencial à preservação, manutenção e promoção da Saúde. O acesso ao medicamento representa um importante fator de inclusão social que depende da disponibilidade do fármaco – princípio ativo contido no medicamento e que em 85% dos casos é de origem sintética. Neste cenário, a importância do saber-fazer fármacos e medicamentos passa a representar um componente estratégico para o pleno exercício da soberania de nosso País. A universalização do acesso ao medicamento, para o cumprimento do preceito de nossa Carta Magna de 1988, quanto ao direito de todos os brasileiros e brasileiras à Saúde, depende, mais do que possa parecer, deste componente.

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Barreiro, E. J.*

Rev. Virtual Quim., **2009**, 1 (1), 18-26. Data de publicação na Web: 30 de Janeiro de 2009

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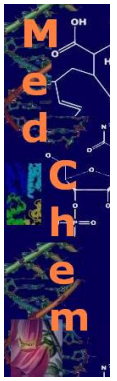

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Diapositivo 38

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A recente criação da PG (M&D) em Farmacologia e Química Medicinal ilustra nova perspectiva de horizonte na PG da UFRJ, pois é a primeira com o perfi desta proposta interdisciplinar na AL.l

Eliezer J. Barreiro; 04/03/2010