

PROCESS NMR ASSOCIATES

Survey of Low Field NMR Spectrometer Platforms for Successful Screening of Sexual Enhancement and Weight Loss Supplements for Adulteration with Drugs and Drug Analogs

John Edwards and Paul Giammatteo
Process NMR Associates, LLC, Danbury, CT

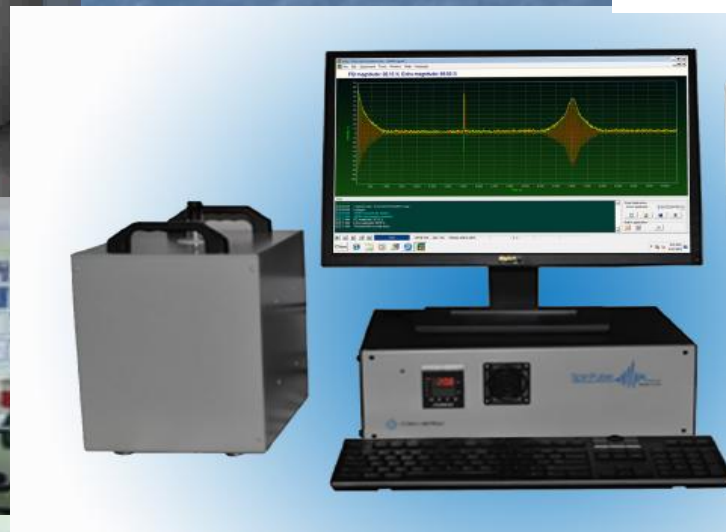
Kristie Adams and Anton Bzhelyansky
U. S. Pharmacopeial Convention, Rockville MD

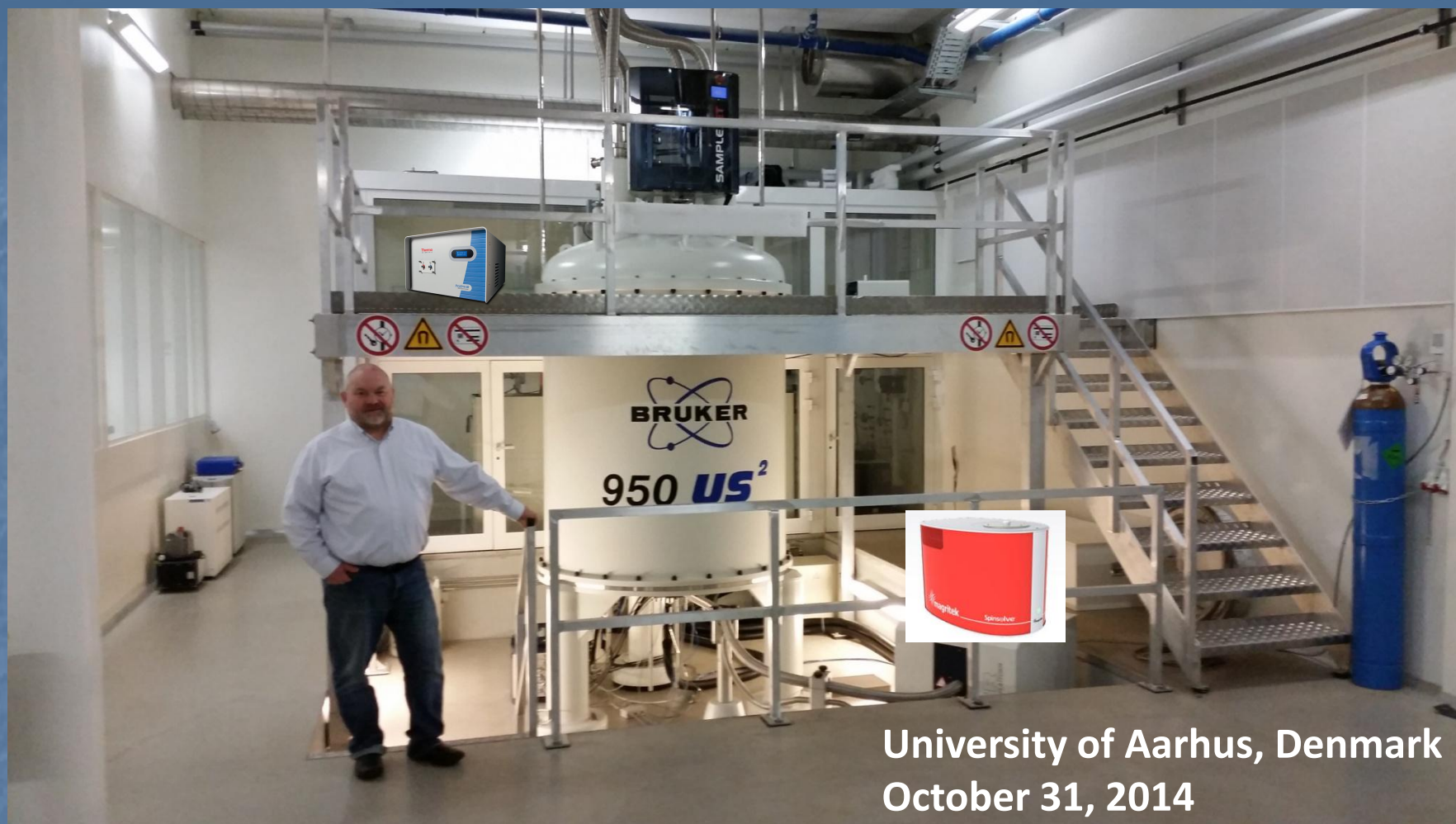
Presented at the Carolina NMR Symposium, November 6 2014
David H. Murdock Research Institute, Kannapolis, NC



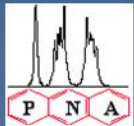
Process NMR
Associates, LLC

NMR Systems





University of Aarhus, Denmark
October 31, 2014



PROCESS NMR ASSOCIATES

Cryogen-Free, 110V, "Portable" NMR Systems



Spinsolve™

42 MHz NMR
3-5 mm Samples
Lab Only



60 MHz NMR
3-5 mm Samples
Lab Only



60 MHz NMR
3-5 mm Samples
Lab Only



MobiLab™ SPECTRA 2T

85+ MHz NMR
3-5 mm Samples
Lab Only

nanalysis

NMReady 60

60 MHz NMR
3-5 mm Samples
Lab Only



Picospin 45 and 80

45 MHz and 82 MHz NMR
300 micron capillary injection
Lab Only

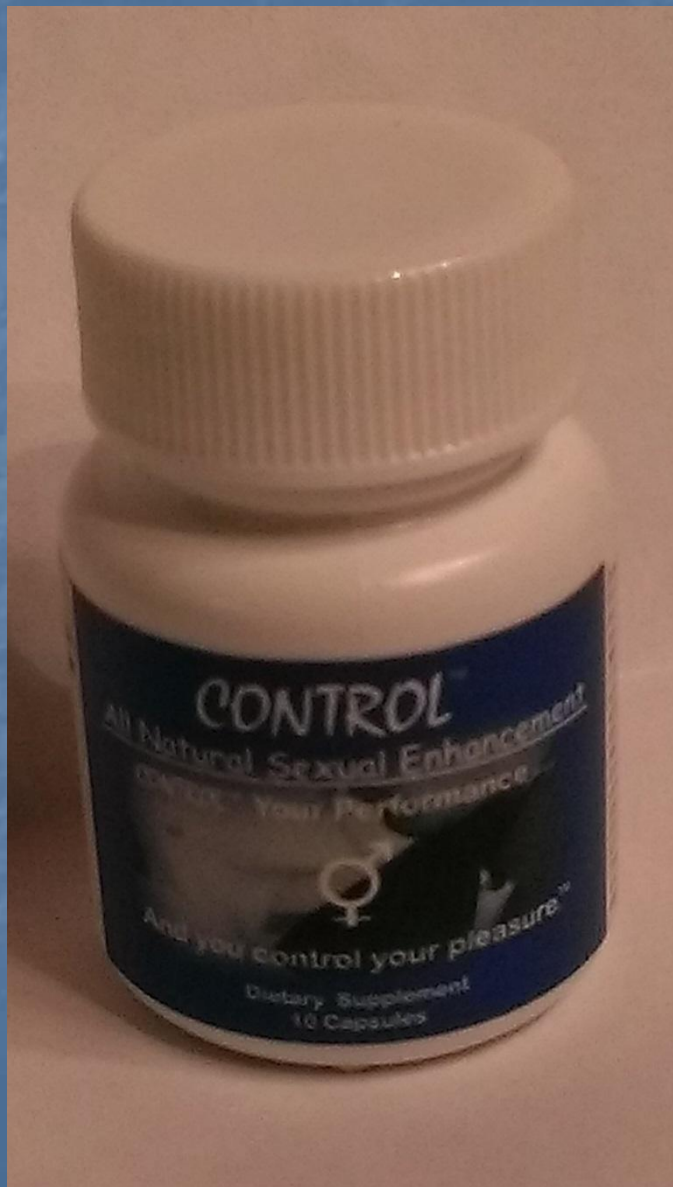
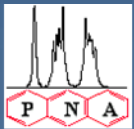


60 MHz NMR
3-10 mm Samples
Lab or On-Line



aspectimaging

60 MHz NMR
3-10 mm Samples
Lab or On-Line



Question:

Why is this competitors product so good?

Ingredients : Oyster, Barberry, Dextrose, Snow Lotus, Bombyx Mori L, Ginger Root, Salfron Crocus.

Anton Quote: “May be just saw dust”

Sample preparation:

Extract with 20:80 D₂O:CD₃CN

Centrifuge or Settle

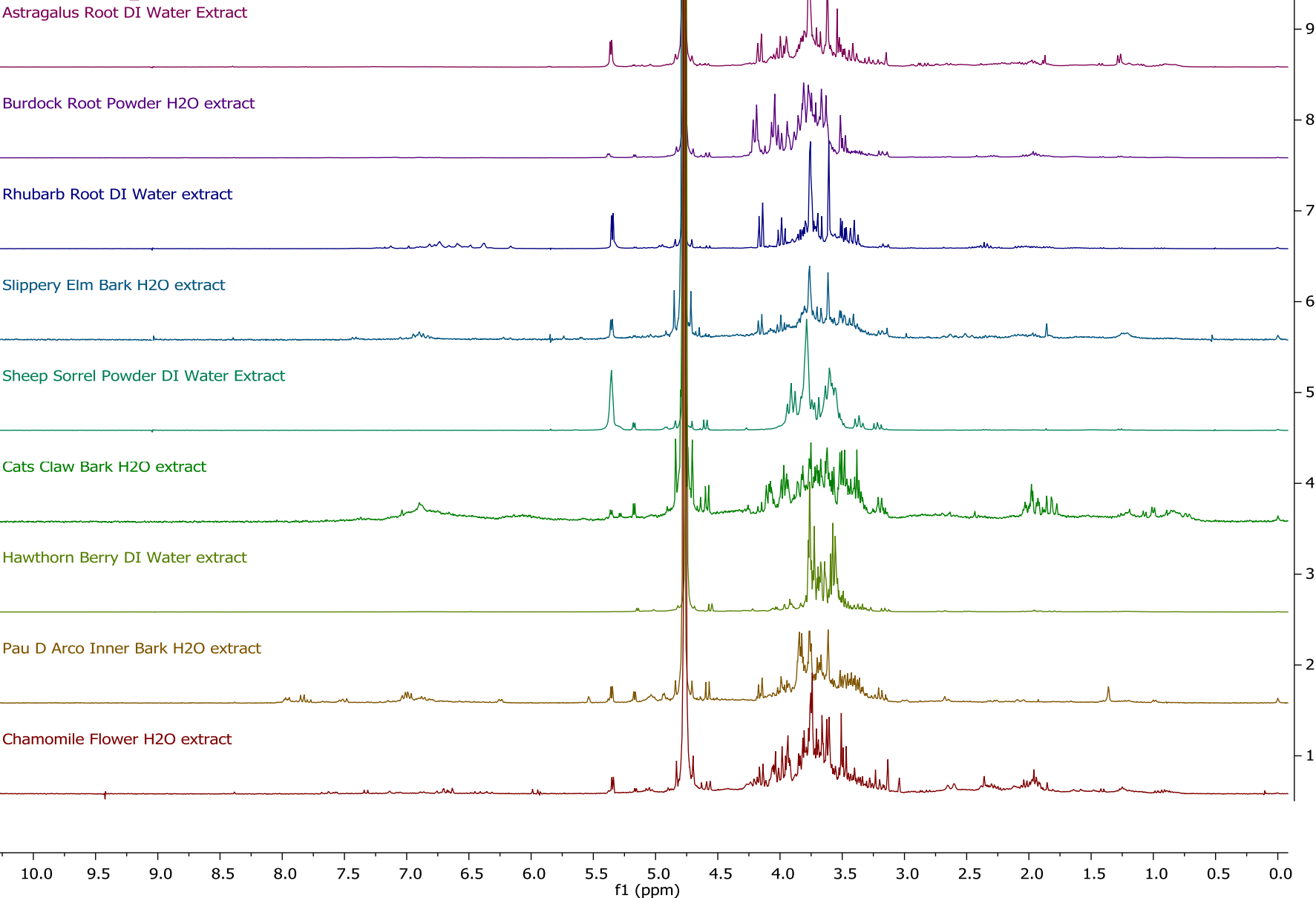
Supernatant analyzed.

Answer:

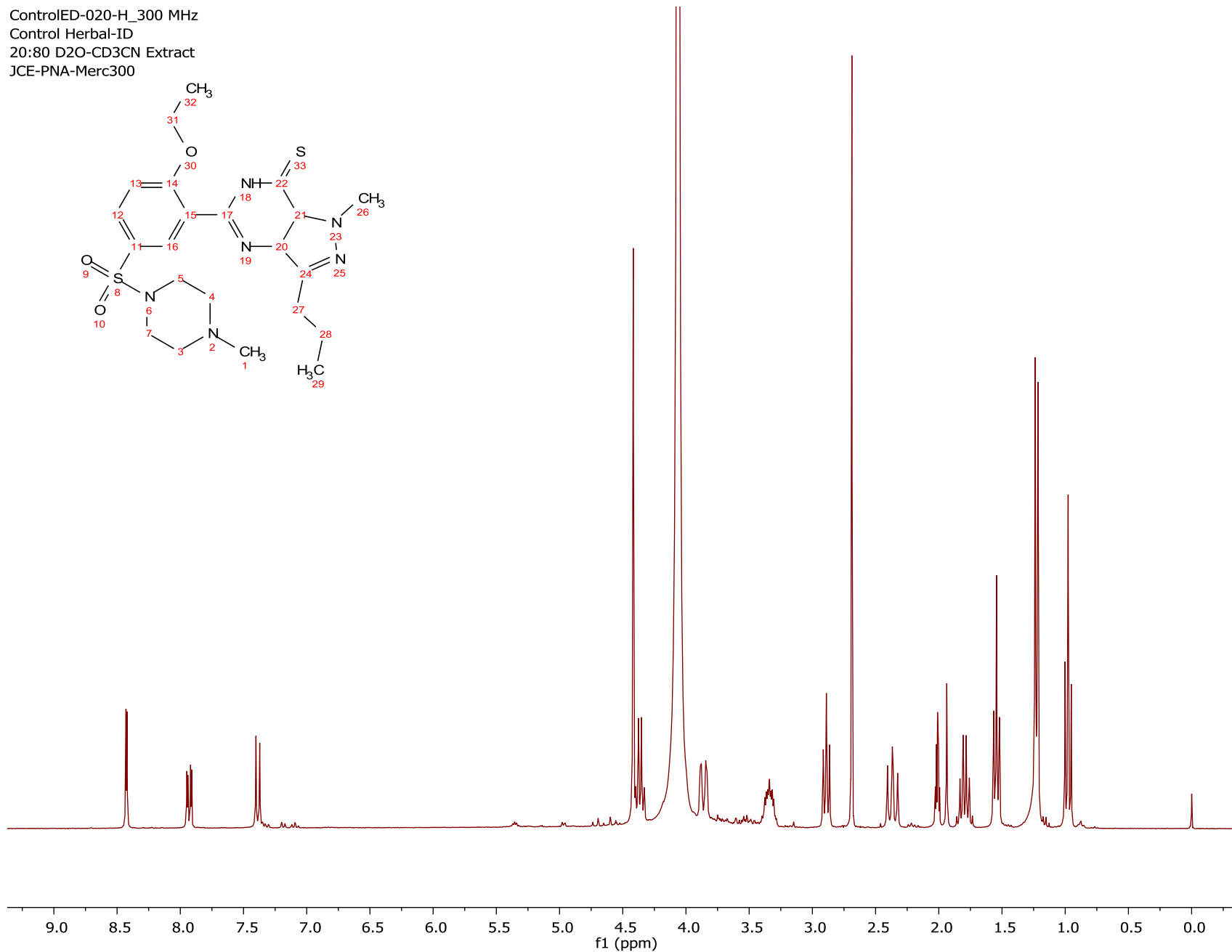
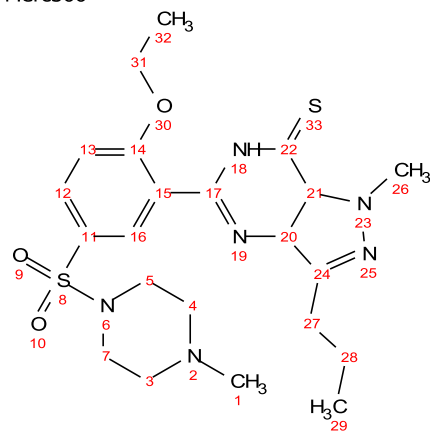
Also contained ~10 wt% Sulfoildenafilafil

A Viagra Analog

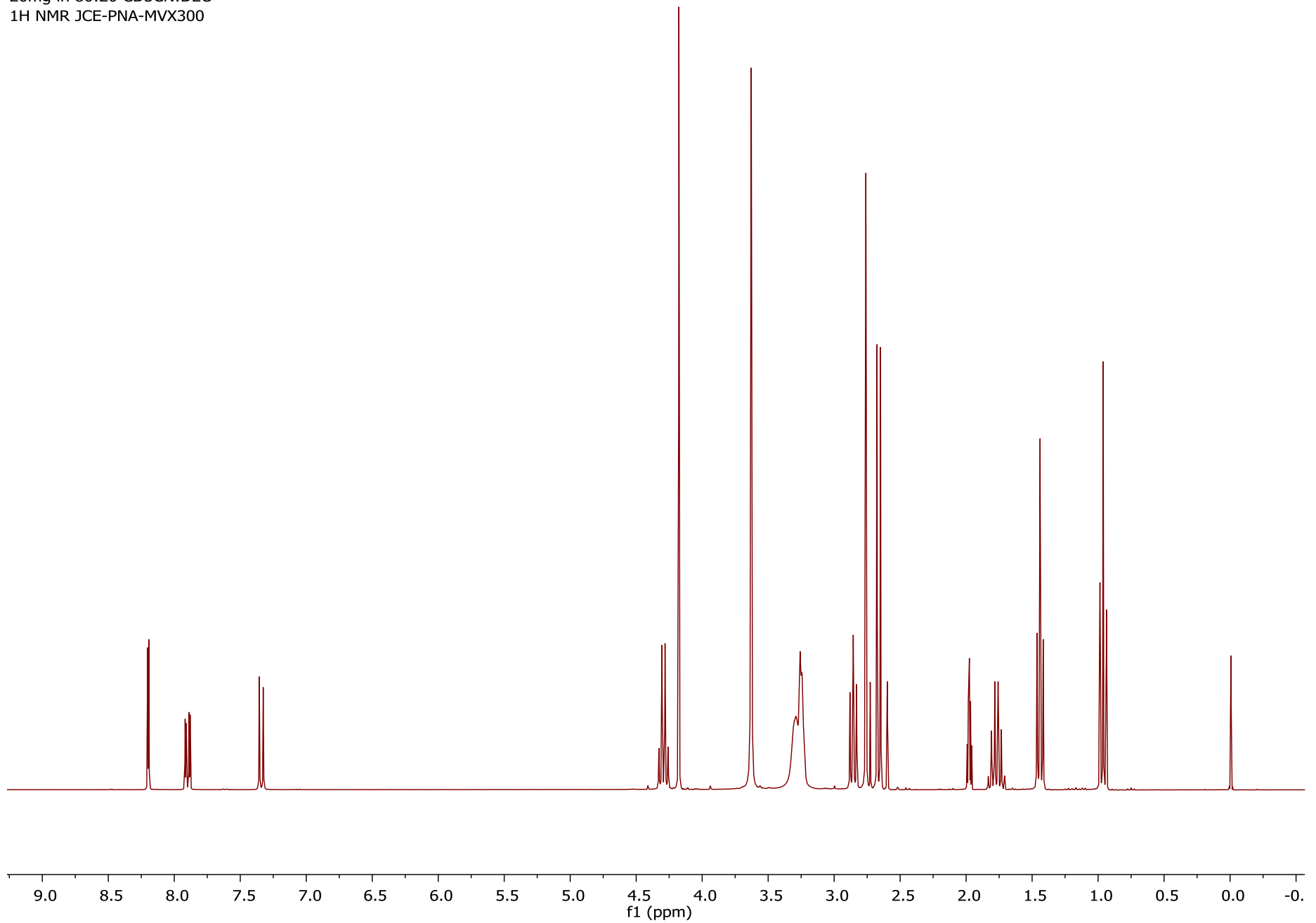
Typical Herbal Extracts



ControlED-020-H_300 MHz
Control Herbal-ID
20:80 D2O-CD3CN Extract
JCE-PNA-Merc300

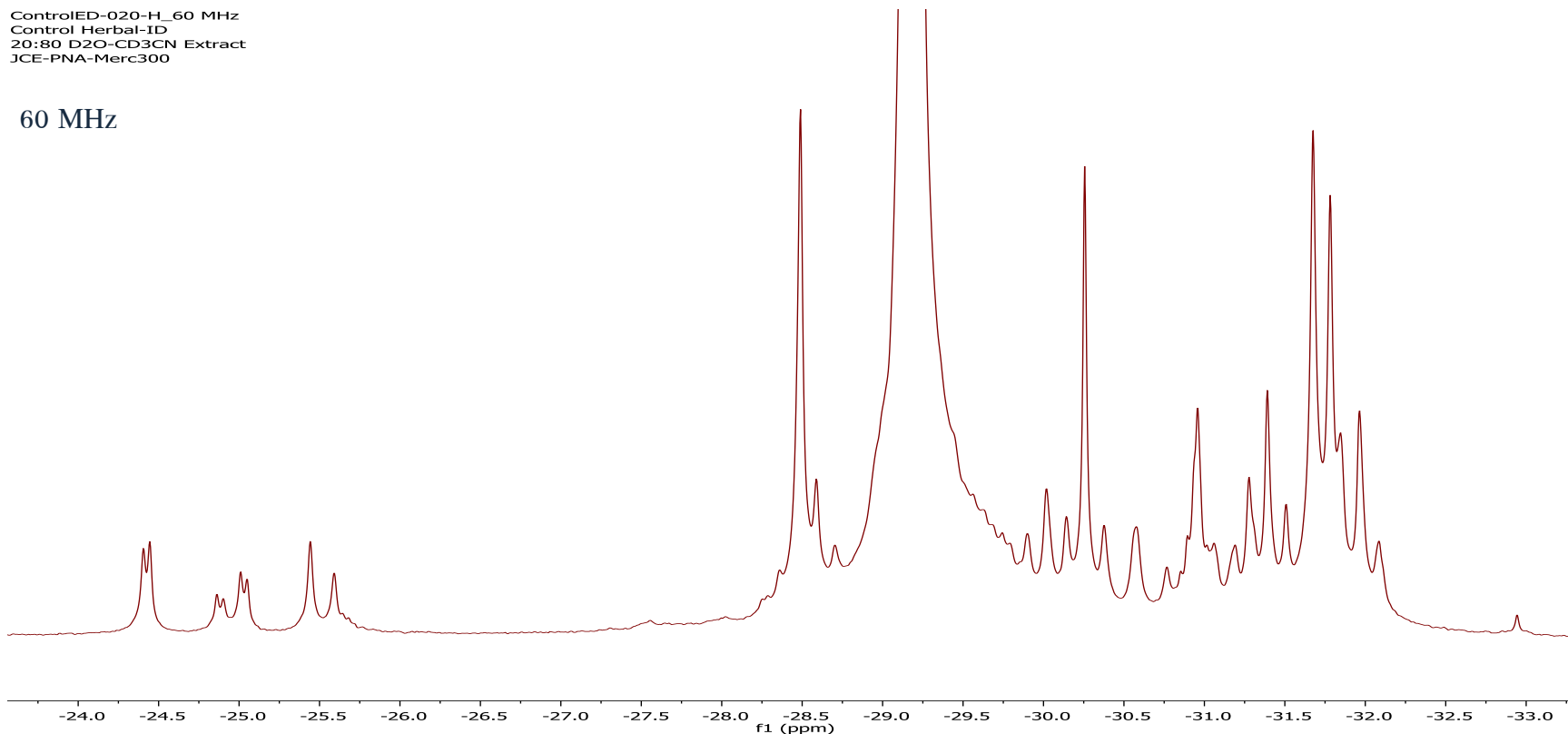


USP-028-H
USP-028-H
Sildenafil
20mg in 80:20 CD3CN:D2O
1H NMR JCE-PNA-MVX300



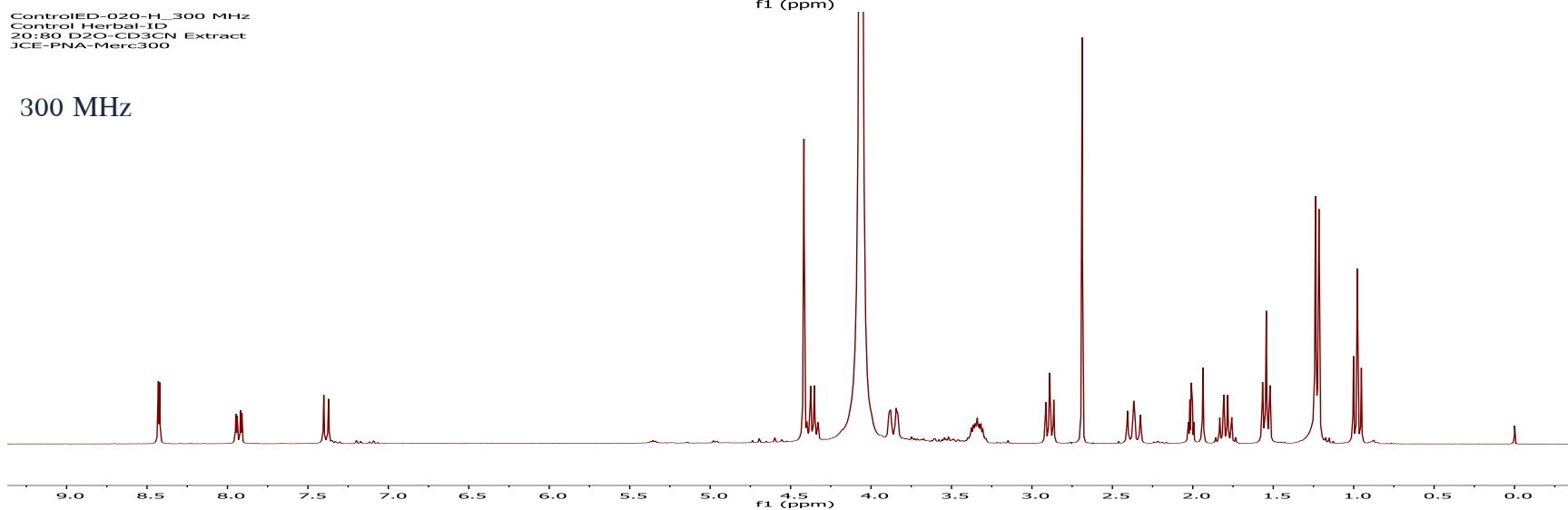
ControlIED-020-H_60 MHz
Control Herbal-ID
20:80 D2O-CD3CN Extract
JCE-PNA-Merc300

60 MHz



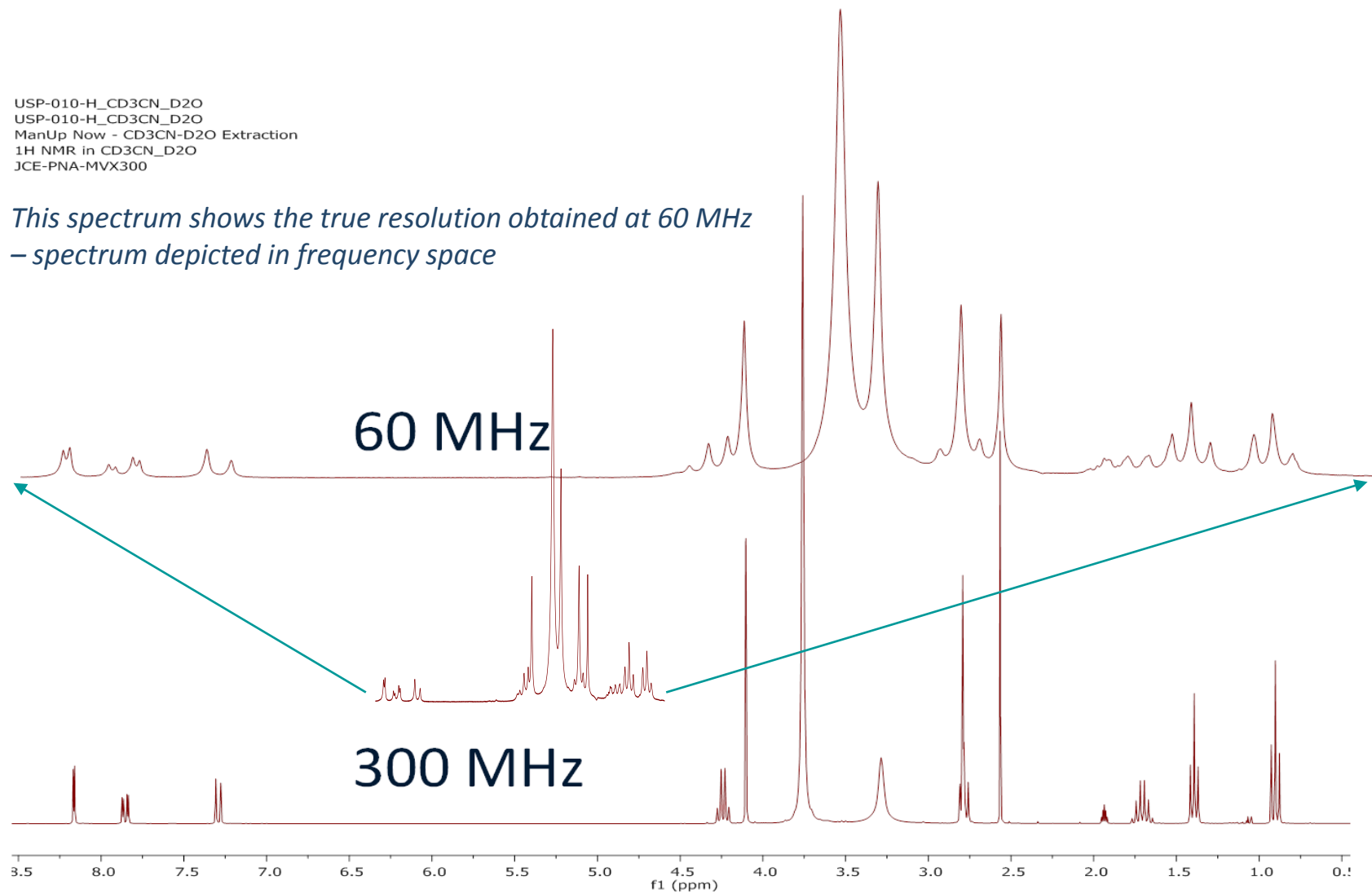
ControlIED-020-H_300 MHz
Control Herbal-ID
20:80 D2O-CD3CN Extract
JCE-PNA-Merc300

300 MHz



USP-010-H_CD3CN_D2O
USP-010-H_CD3CN_D2O
ManUp Now - CD3CN-D2O Extraction
1H NMR in CD3CN-D2O
JCE-PNA-MVX300

*This spectrum shows the true resolution obtained at 60 MHz
– spectrum depicted in frequency space*



Comparison of 300 and 60 MHz NMR of ManUp Now Herbal Supplement –acetonitrile-D₂O extract

Simple Mixture Analysis

Analyze Settings Report Libraries

Analysis Data Result

Mixture

Library: D:/MNOVA/USP/ED Herbals

Name: ED Herbals

Description: PDE5i in Herbal Supplements

Sample Details

Sample ID: herbal ED-300 Weight(mg): 95.2

Reference Concentration: Reference Weight(mg): 25.9

Metadata

SOP: 1H qNMR - 300 MHz - Maleic

Investigator: John Edwards

Customer: XXX

Customer Sample Number: XXX

Comments: XXX

Experiment

Name: ED Herbals

Description: PDE5i in Herbal Supplements

Units: wt%

Compound	Type	Mol. Weight	Color	Spectrum
Sulfoaidenafil	Compound	504.67	Blue	1
Maleic Acid	Ref	116.07	Red	1
Sulfoaidenafil-60	Compound	504.67	Blue	1

Compound Editor

Name: Sulfoaidenafil-60

Color: Blue Spectrum N°: 1 Molecular Weight: 504.67

Type: Compound Acceptable Limit From: To:

Formula

Formula Editor

100*(RW*((I1+I2+I3)/(NN1+NN2+NN3))*MW)/(IR1/(NNR1)*MWR*SW)

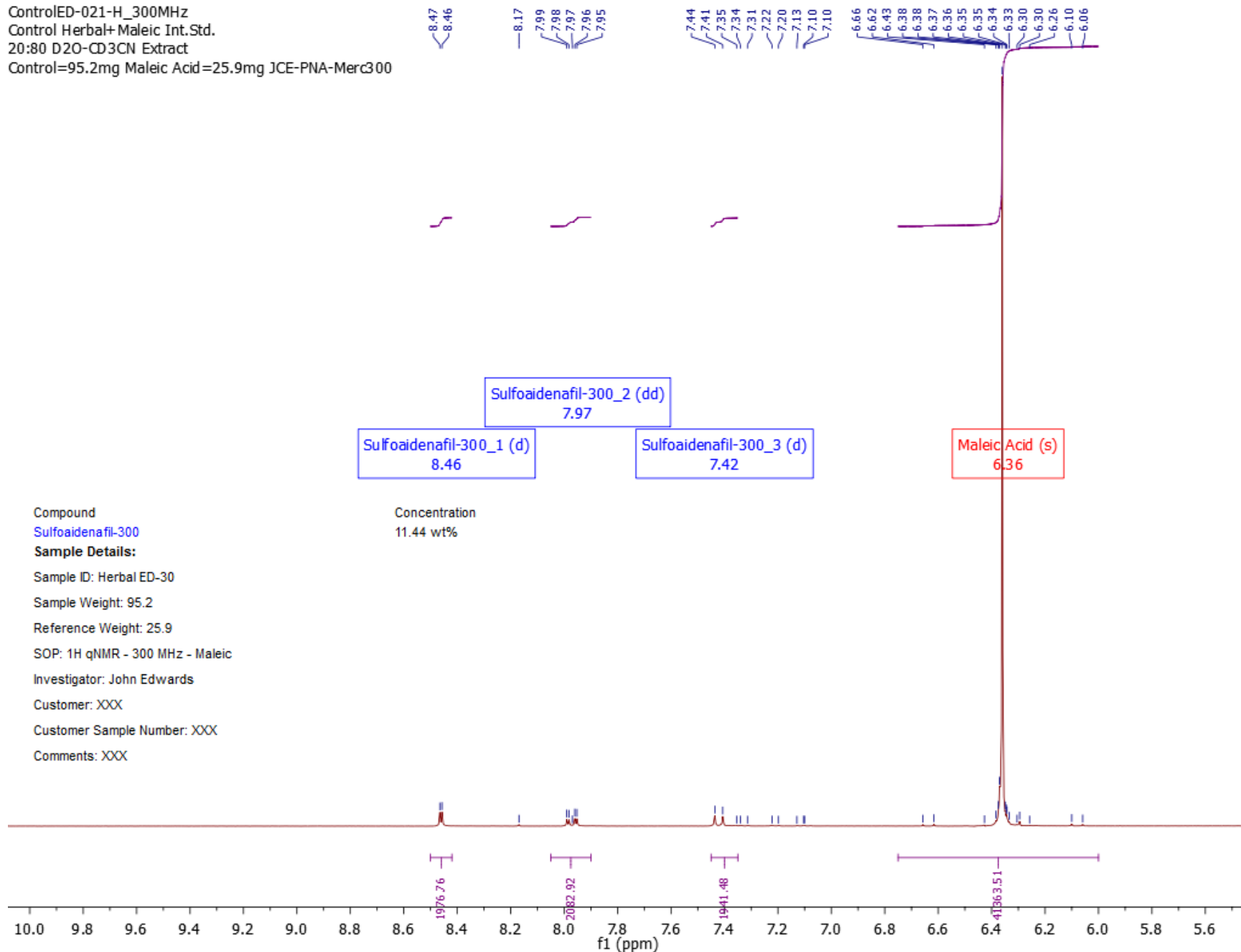
Ranges

	From	To	NN
1	8.66	8.42	1
2	8.15	7.82	1

OK Cancel

$$\text{Component Wt\%} = 100 \times (\text{Component Molar Integral} / \text{Std Molar Integral}) \times (\text{Wt Std} / \text{Wt Sample}) \times (\text{Component Mw} / \text{Std Mw})$$

ControlED-021-H_300MHz
 Control Herbal+ Maleic Int.Std.
 20:80 D2O-CD3CN Extract
 Control=95.2mg Maleic Acid=25.9mg JCE-PNA-Merc300



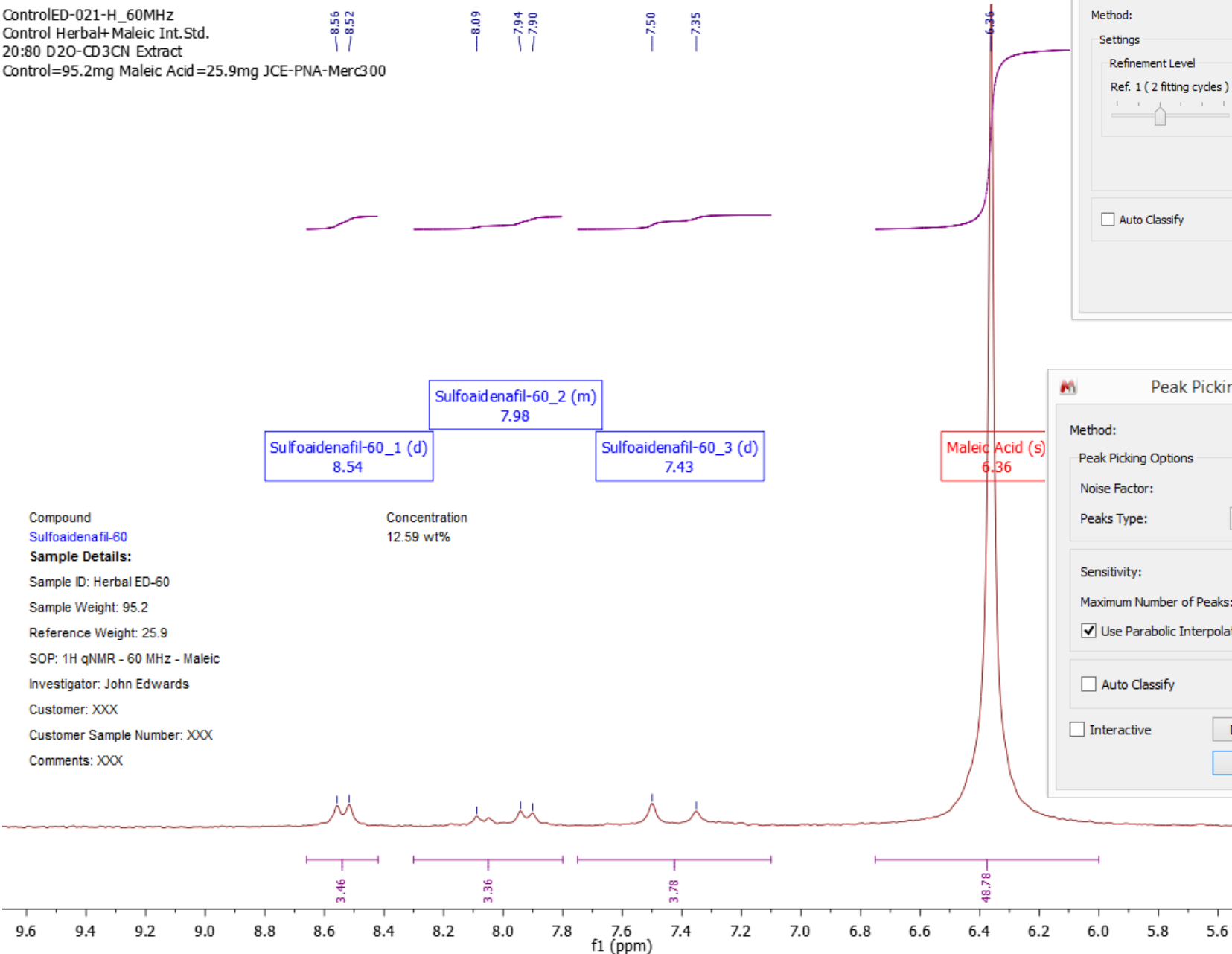
Compound
 Sulfoaidenafil-300
Sample Details:
 Sample ID: Herbal ED-30
 Sample Weight: 95.2
 Reference Weight: 25.9
 SOP: 1H qNMR - 300 MHz - Maleic
 Investigator: John Edwards
 Customer: XXX
 Customer Sample Number: XXX
 Comments: XXX

Concentration
 11.44 wt%

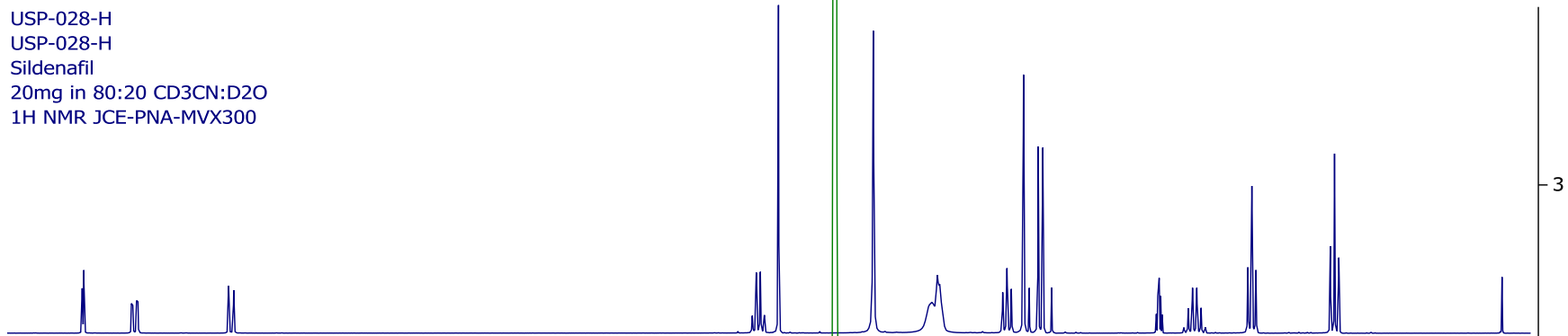
ControlED-021-H_60MHz
 Control Herbal+ Maleic Int.Std.
 20:80 D2O-CD3CN Extract
 Control=95.2mg Maleic Acid=25.9mg JCE-PNA-Merc300

Compound
 Sulfoaidenafil-60
Sample Details:
 Sample ID: Herbal ED-60
 Sample Weight: 95.2
 Reference Weight: 25.9
 SOP: 1H qNMR - 60 MHz - Maleic
 Investigator: John Edwards
 Customer: XXX
 Customer Sample Number: XXX
 Comments: XXX

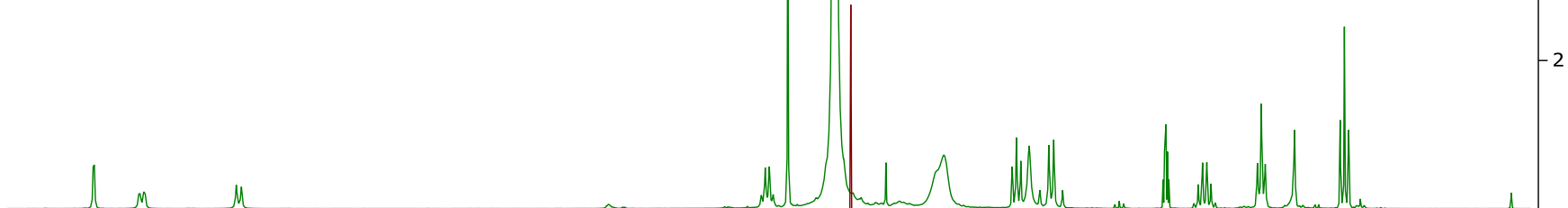
Concentration
 12.59 wt%



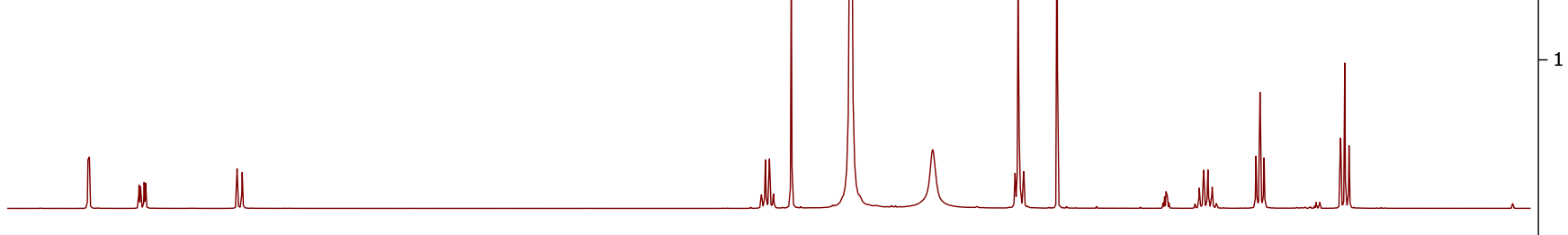
USP-028-H
USP-028-H
Sildenafil
20mg in 80:20 CD3CN:D2O
1H NMR JCE-PNA-MVX300



USP-011-H_CD3CN_D2O
USP-011-H_CD3CN_D2O
Stree Overlord - CD3CN-D2O Extraction
1H NMR in CD3CN_D2O
JCE-PNA-MVX300

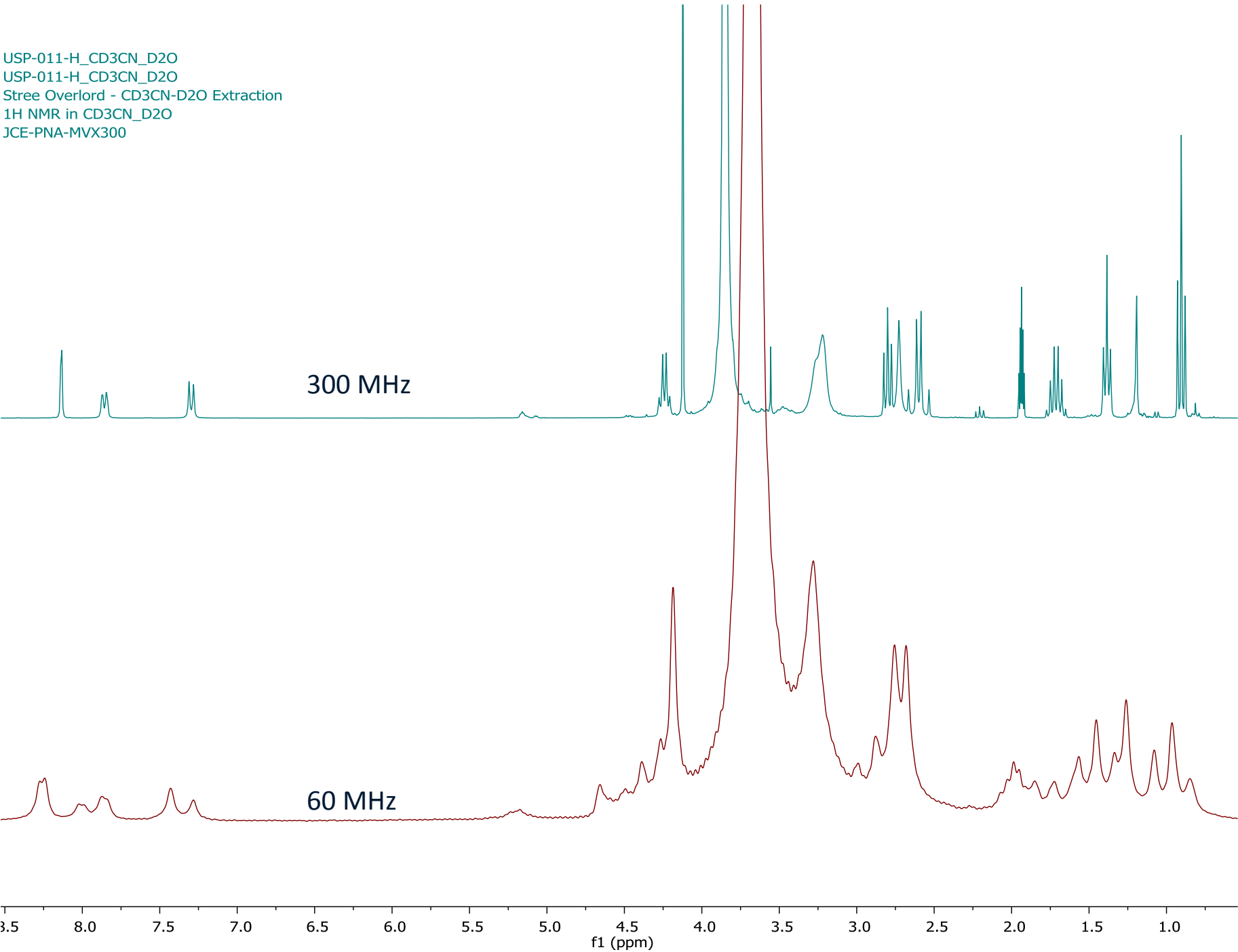


USP-010-H_CD3CN_D2O
USP-010-H_CD3CN_D2O
ManUp Now - CD3CN-D2O Extraction
1H NMR in CD3CN_D2O
JCE-PNA-MVX300

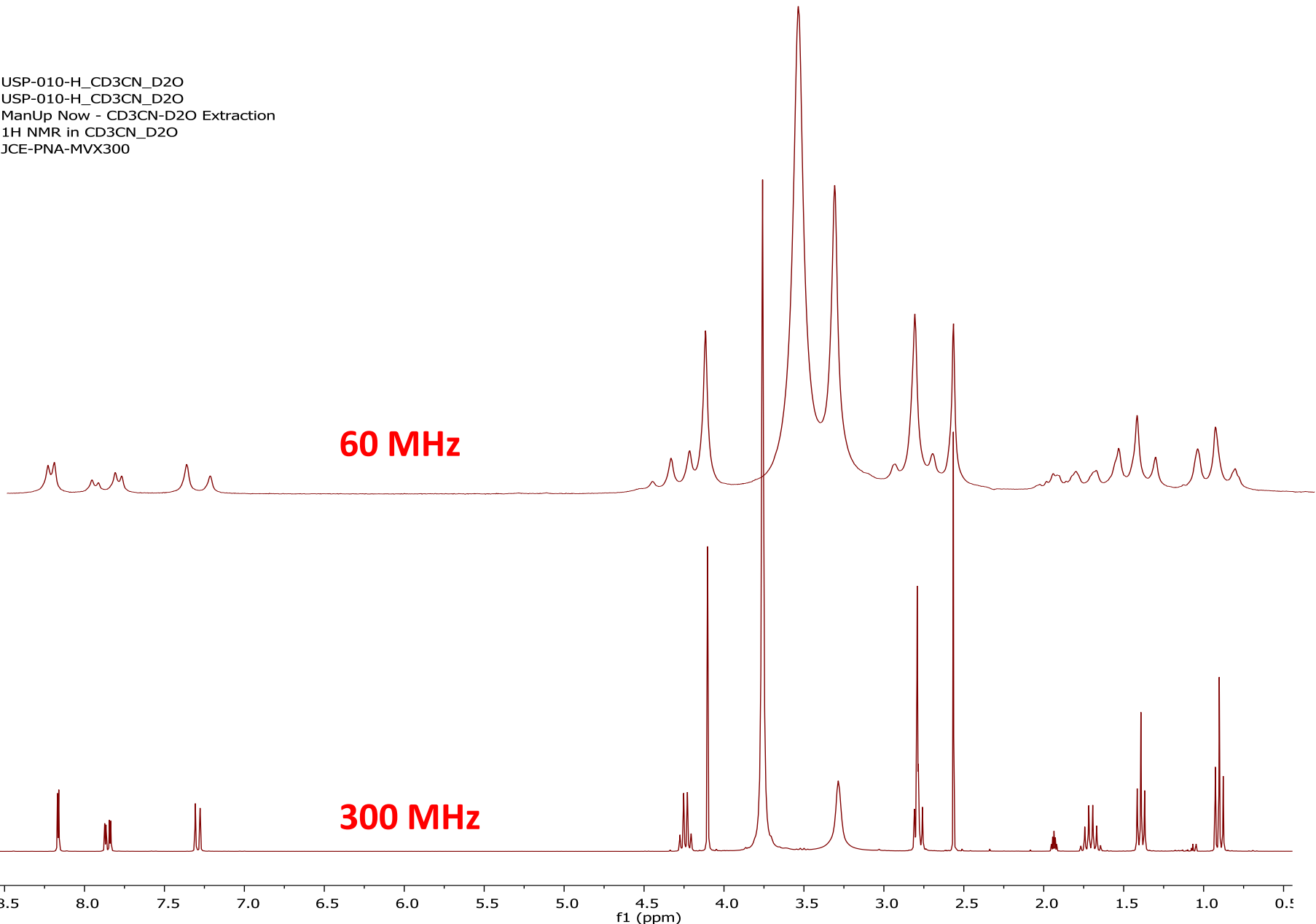


8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

USP-011-H_CD3CN_D2O
USP-011-H_CD3CN_D2O
Stree Overlord - CD3CN-D2O Extraction
1H NMR in CD3CN_D2O
JCE-PNA-MVX300



USP-010-H_CD3CN_D2O
USP-010-H_CD3CN_D2O
ManUp Now - CD3CN-D2O Extraction
1H NMR in CD3CN_D2O
JCE-PNA-MVX300

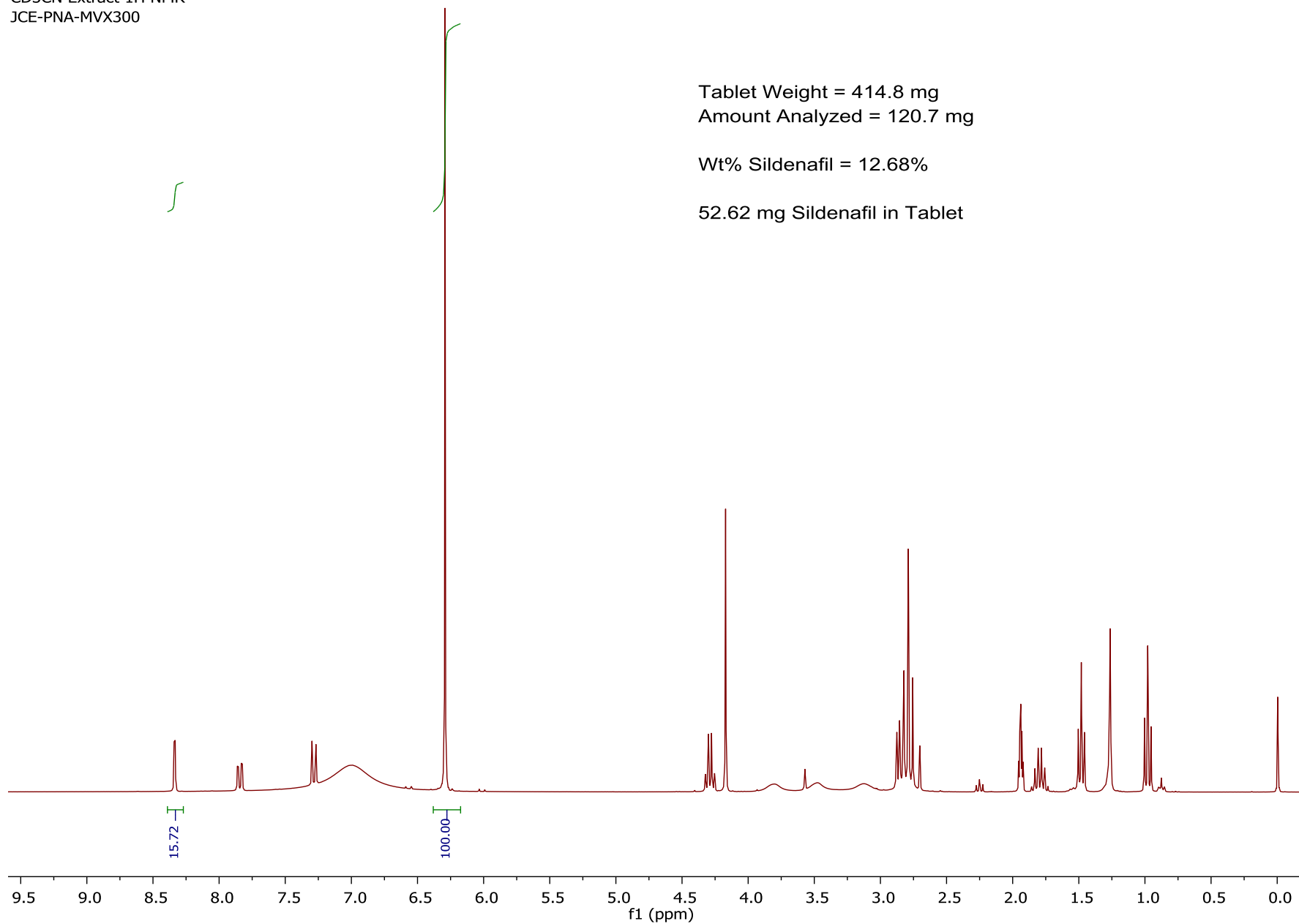


USP-PDE5i-011-H-qNMR
USP-PDE5i-011-H-qNMR
Stree Overlord 120.7mg + 11.2mg Maleic Acid
CD3CN Extract 1H NMR
JCE-PNA-MVX300

Tablet Weight = 414.8 mg
Amount Analyzed = 120.7 mg

Wt% Sildenafil = 12.68%

52.62 mg Sildenafil in Tablet



Component Wt% = 100 x (Component Molar Integral / Std Molar Integral) x (Wt Std / Wt Sample) x (Component Mw / Std Mw)

USP-PDE5i-010-H-qNMR
USP-PDE5i-010-H-qNMR
Man Up Now + 16.9mg Maleic Acid
CD3CN Extract 1H NMR
JCE-PNA-MVX300

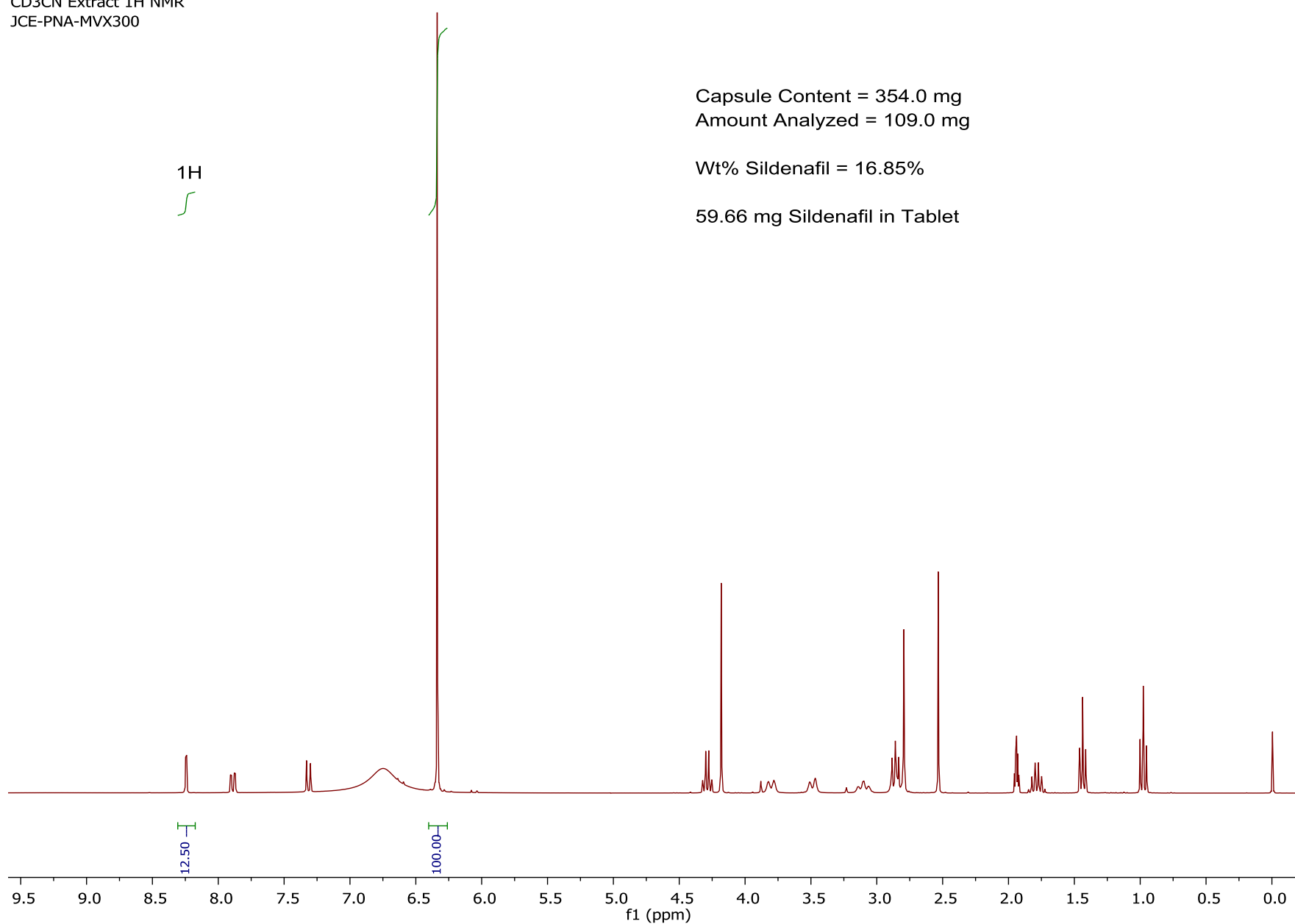
MA

1H

Capsule Content = 354.0 mg
Amount Analyzed = 109.0 mg

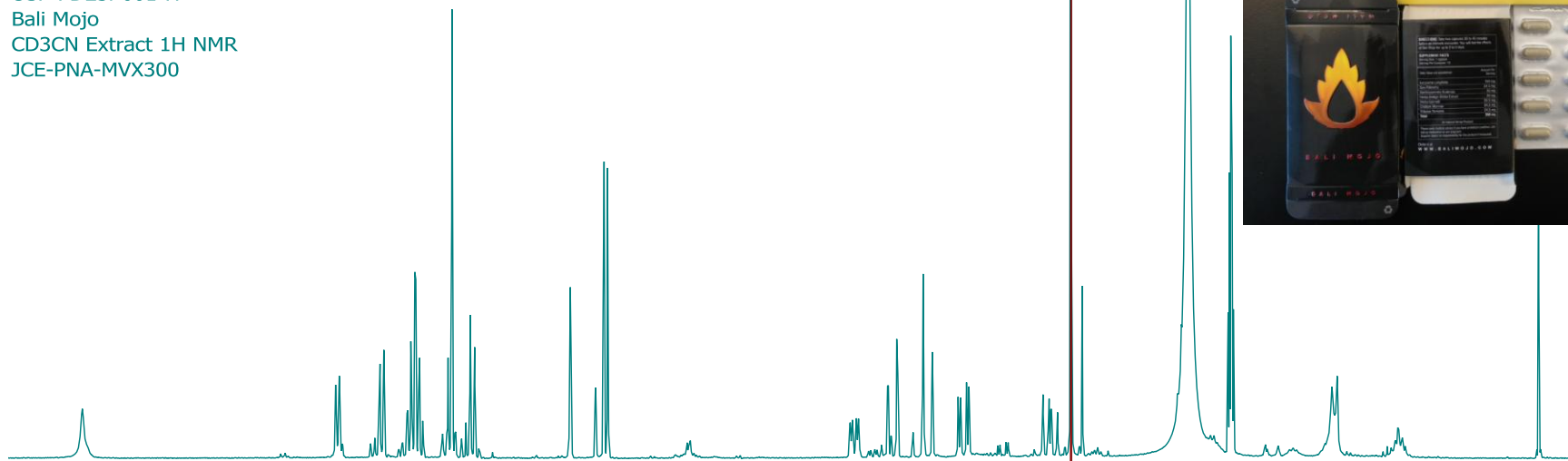
Wt% Sildenafil = 16.85%

59.66 mg Sildenafil in Tablet

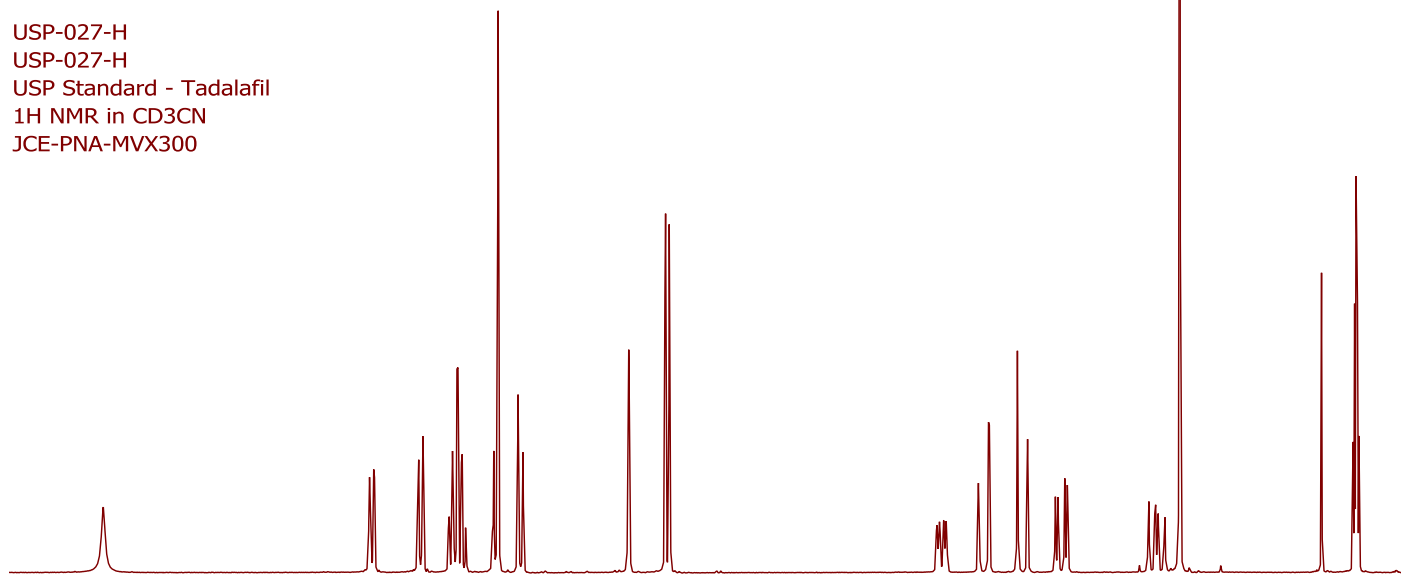


Component Wt% = 100 x (Component Molar Integral / Std Molar Integral) x (Wt Std / Wt Sample) x (Component Mw / Std Mw)

USP-PDE5i-001-H
USP-PDE5i-001-H
Bali Mojo
CD3CN Extract 1H NMR
JCE-PNA-MVX300



USP-027-H
USP-027-H
USP Standard - Tadalafil
1H NMR in CD3CN
JCE-PNA-MVX300



9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



DIRECTIONS: Take two capsules 30 to 40 minutes before an intimate encounter. You will feel the effects of Bali Mojo for up to 2 to 3 days.

SUPPLEMENT FACTS

Serving Size: 1 capsule
Serving Per-Container: 10

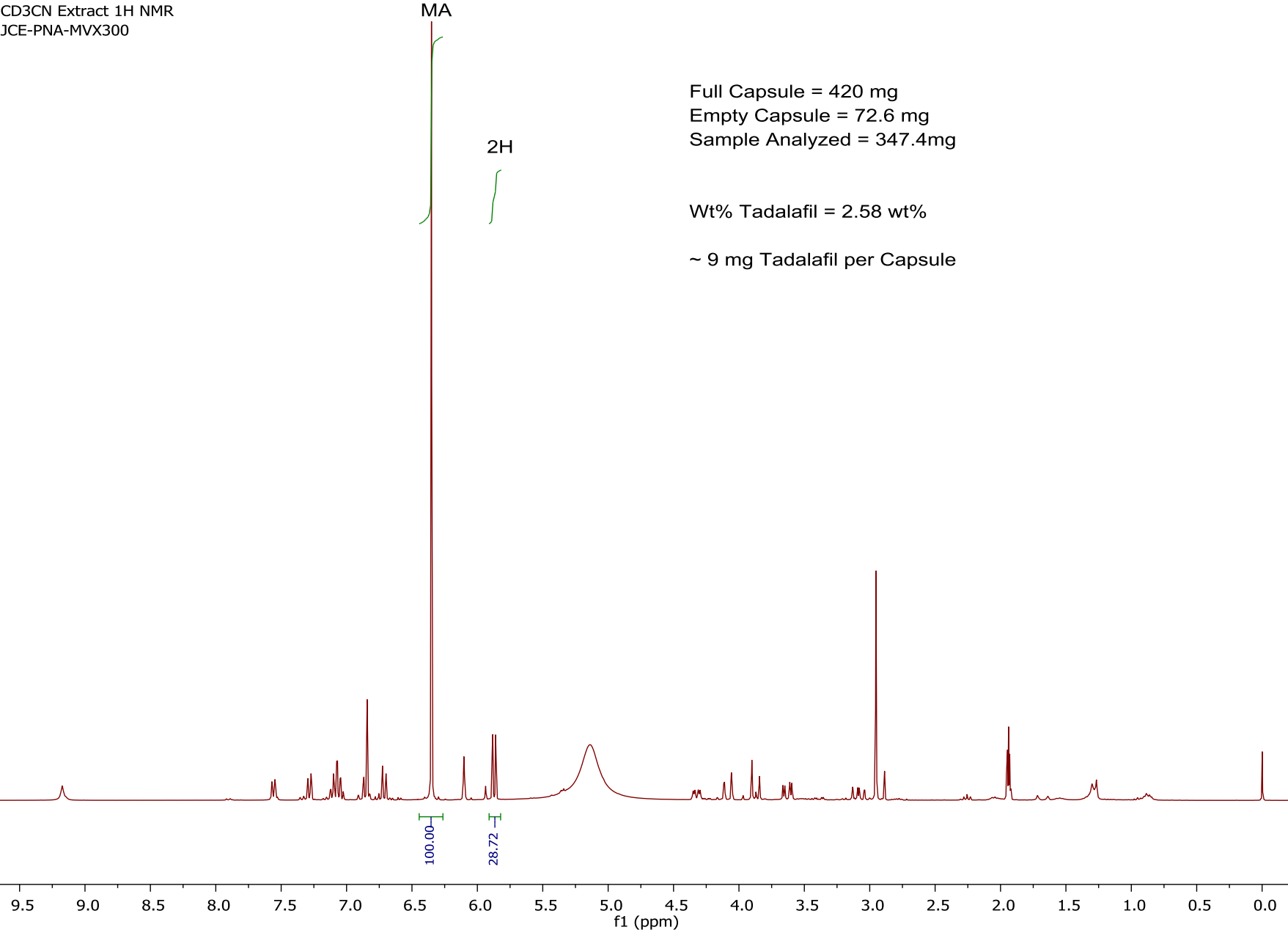
Daily Value not established	Amount Per Serving
Eurycoma Longifolia	154 mg
Saw Palmetto	24.5 mg
Xanthoparmelia Scabrosa	49 mg
Herba Ginkgo Biloba Extract	49 mg
Herba Epimedi	24.5 mg
Cnidium Monnier	24.5 mg
Tribulus Terrestris	24.5 mg
Total	350 mg

All Natural Herbal Product.

Please seek medical advice if you have a medical condition, are taking medication or are pregnant.
Supplier bears no responsibility for the product if misused.

Order it at:
WWW.BALIMOJO.COM

USP-PDE5i-001-H-qNMR
USP-PDE5i-001-H-qNMR
Bali Mojo + 9.3mg Maleic Acid
CD3CN Extract 1H NMR
JCE-PNA-MVX300



Full Capsule = 420 mg
Empty Capsule = 72.6 mg
Sample Analyzed = 347.4mg

Wt% Tadalafil = 2.58 wt%
~ 9 mg Tadalafil per Capsule

Component Wt% = 100 x (Component Molar Integral / Std Molar Integral) x (Wt Std / Wt Sample) x (Component Mw / Std Mw)



Sample Preparation

Qualitative:

Open Capsule or Grind Tablet

Place ~200 mg sample in 2 dram vial

Add 700 μ l 99.8% CD_3CN (\$3)

Mix Thoroughly (eg. Vortex) Allow to settle

Pipette supernatant liquid into an Economy 5mm tube (\$0.85) and allow solids to settle.

Quantitative:

Weigh Capsule contents to nearest 0.1mg

Weigh sample into vial to nearest 0.1 mg

Add appropriate internal standard weighed to nearest 0.1mg

300 MHz ^1H NMR

5 mm NMR Tube

Pulse Width: 45 Degree Tip Angle

Spectral Width = 8 kHz

Acquisition Time = 3.5 seconds

Relaxation Delay = 7 Seconds (Qual)
= 20 seconds (Quant)

Averages: 16-256 – S/N Decision (

60 MHz ^1H NMR

Same as above except:

Spectral Width = 2 kHz

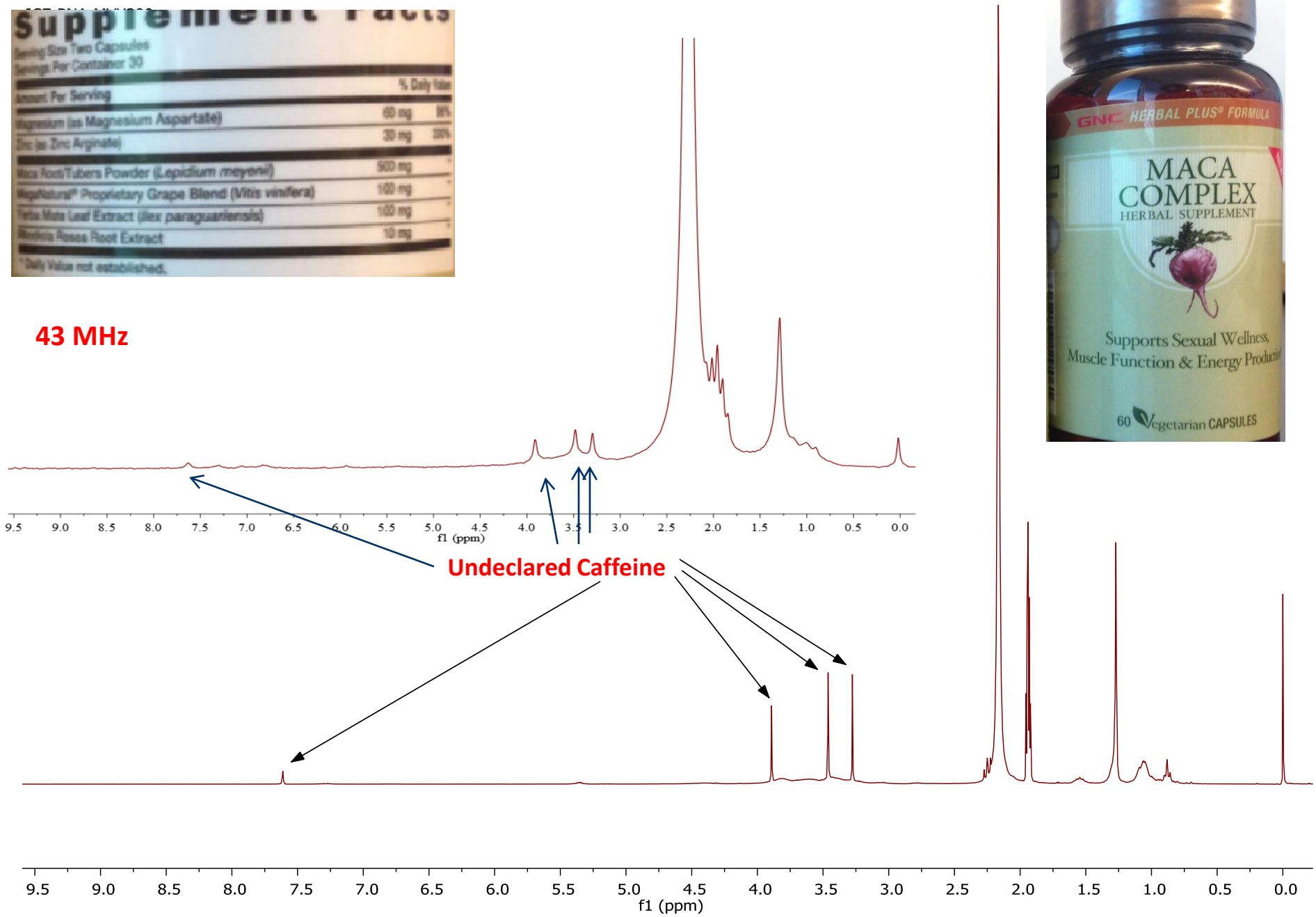
Pulse Averages – 32-256

Product Name	Distributor	Supplier Name	Dosage Form	Supplement Facts	Dose
Bulgarian Tribulus	Ultimate Nutrition	Ultimate Nutrition, Inc	Capsule	Tribulus Blend extract [fruit] and tribulus [aerial parts]	Tribulus 750 mg
Men's Staminol Rapid Surge	GNC	General Nutrition Corporation	Caplet	Niacin	25 mg
				Sexual Health Circulatory Blend	300 mg
				Maca Root Powder	
				Horny Goat Weed Extract	
				Damiana Leaf Extract	
				Cayenne Fruit Powder	
				Du-Zhong Bark Extract	
				Yohimbe Bark Extract	112.5 mg
				Caffeine Anhydrous	100 mg
				Ginkgo biloba leaf Extract	50 mg
Maca Complex	GNC	General Nutrition Corporation	Capsule	Res-Vida (trans-resveratrol)	30 mg
				DHEA	25 mg
				Magnesium (as Mg Aspartate)	60 mg
				Zinc (as Zn Alginate)	30 mg
				Maca Roots/Tubers Powder	500 mg
Vigorexin	Online	Vigorexin, LLC	Capsule	MegaNutra Proprietary Grape Blend	100 mg
				Yerba Mate Leaf Extract	100 mg
				Rhodiola Rose Root Extract	10 mg
				Niacin	45 mg
				Tribulus terrestris, 40% protodioscin, 60% furastanol saponins, 80% total saponins	200 mg
				L-Citrulline	500 mg
				L-Arginine HCl	100 mg
				Arginine AKG 2:1	275 mg
				Eurycoma longifolia Jack, 100:1	100 mg
				Maca Roots/Tubers Powder	5 mg
Yohimbe Herbal Supplement Traditional Male Herb	GNC	General Nutrition Corporation	Capsule	Avena sativa, 10:1	5 mg
				Grape Seed Extract	5 mg
Goldenseal Root Herbal Supplement Extract	GNC	General Nutrition Corporation	Capsule	Yohimbine HCl	3 mg
Horny Goat Weed	GNC	General Nutrition Corporation	Capsule	Yohimbe Bark Extract	(2% 450 mg)
				Yohimbine Alkaloids = 9 mg)	(Minimum 200 mg)
ExtenZe Extended Release Maximum Strength Male Enhancement	GNC	Global Products Management	Liquid Gelcap	5% Hydrastine = 10 mg)	
				Horny Goat Weed Extract	600 mg
				Maca Root Extract	250 mg
				Polypodium vulgare Root Powder	25 mg
				Extenze Multi Active Blend	135 mg
				Yohimbe Extract (Bark)	
				DHEA (98%)	
				Gamma-Aminobutyric Acid (GABA-98%)	
				Niacin	
				Velvet Bean Extract (seed)	
				Tongkat Ali Extract (root)	
				Tribulus Extract (fruit)	
				Extenze Sexual Response Enhancement Blend	223 mg
				Black Pepper extract (fruit)	
				Cnidium Extract (seed)	
				Damiana Extract (leaf)	
				DHEA (98%)	
				Gamma-Aminobutyric Acid (GABA-98%)	
				Korean Ginseng (root)	
				Barrenwort Extract (leaf)	
				L-Arginine HCl (98%)	
				Licorice Extract (root)	
				Muira Puama Extract (bark)	
				Pregnenolone (98%)	
				Tribulus Extract (fruit)	
				Folate (Folic Acid)	
				Yohimbe HCl (98%)	
				Astragalus Extract (root)	
				Niacin	
				Tongat Ali Extract (root)	
				Velvet Bean Extract (seed)	
				Chrysin (98%)	
Bali Mojo	Online	Bali Mojo, Inc.	Capsule	Eurycoma longifolia	154 mg
				Saw Palmetto	24.5 mg
				Xanthoparmelia scabrosa	49 mg
				Herba Ginkgo Biloba Extract	49 mg
				Herba Epimedi	24.5 mg
				Cnidium monnieri	24.5 mg
				Tribulus terrestris	24.5 mg

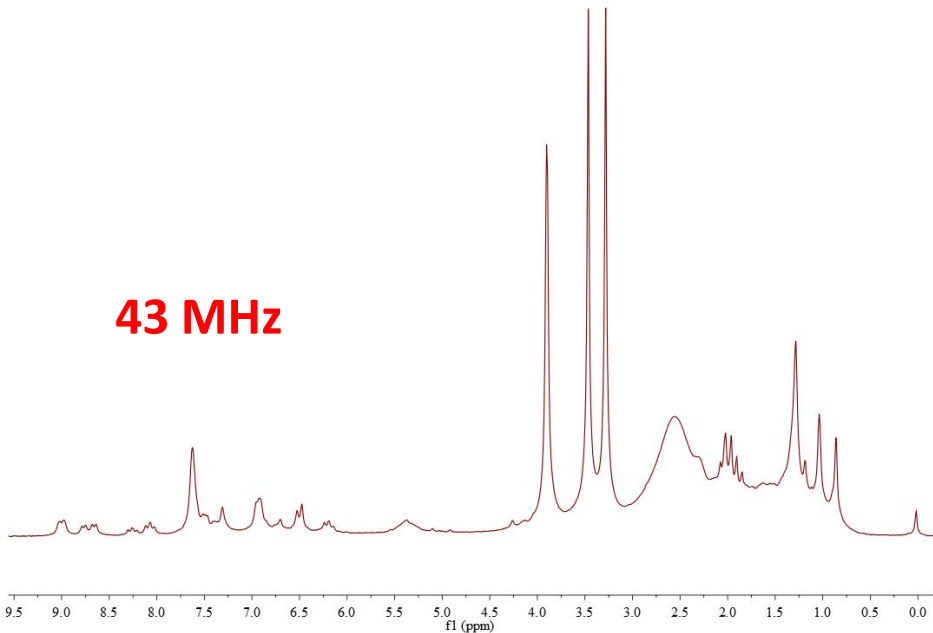
USP-PDE5i-003-H
USP-PDE5i-003-H
Maca
CD3CN Extract 1H NMR

Supplement Facts		
Serving Size Two Capsules		
Servings Per Container 30		
Amount Per Serving		% Daily Value
Magnesium (as Magnesium Aspartate)	60 mg	18%
Zinc (as Zinc Arginate)	30 mg	100%
Maca Root/Tubers Powder (<i>Lepidium meyenii</i>)	900 mg	"
MegaNatural® Proprietary Grape Blend (<i>Vitis vinifera</i>)	100 mg	"
Yucca Mite Leaf Extract (<i>Yucca paraguayensis</i>)	100 mg	"
Rhodola Rosea Root Extract	10 mg	"
* Daily Value not established.		

43 MHz

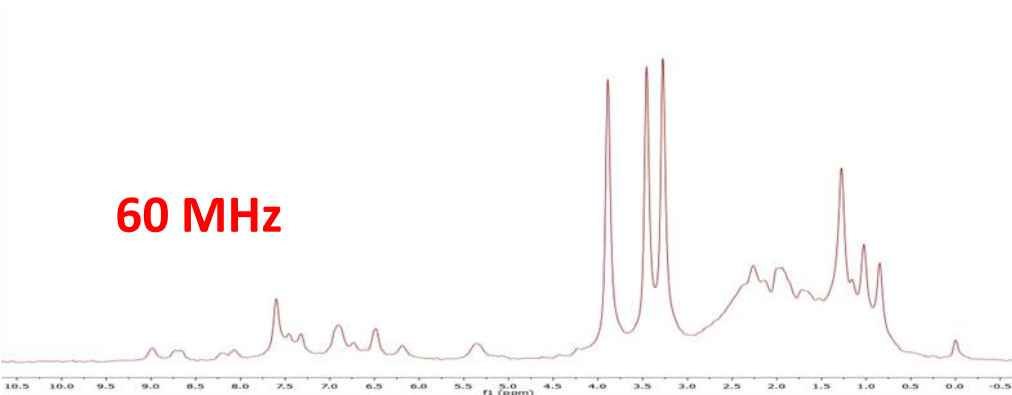


43 MHz



Caffeine

60 MHz



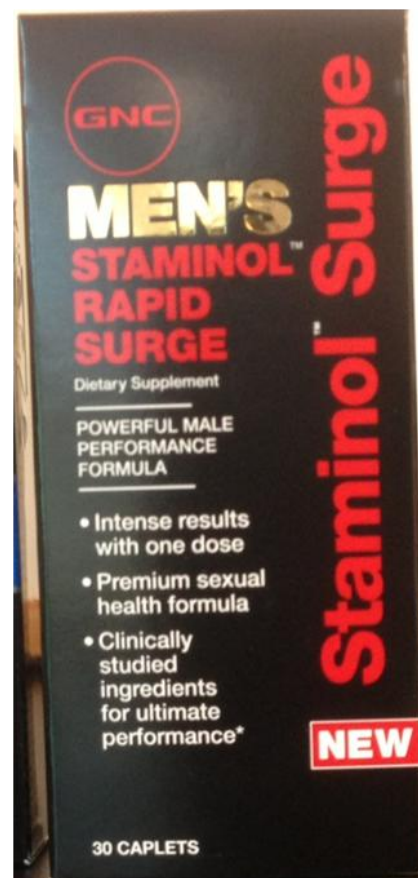
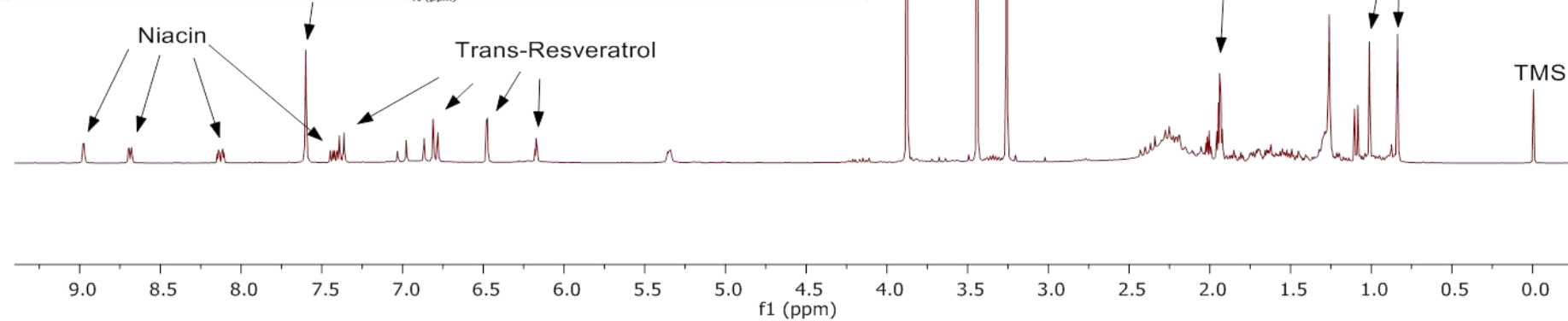
Niacin

Trans-Resveratrol

CD3CN

DHEA

TMS



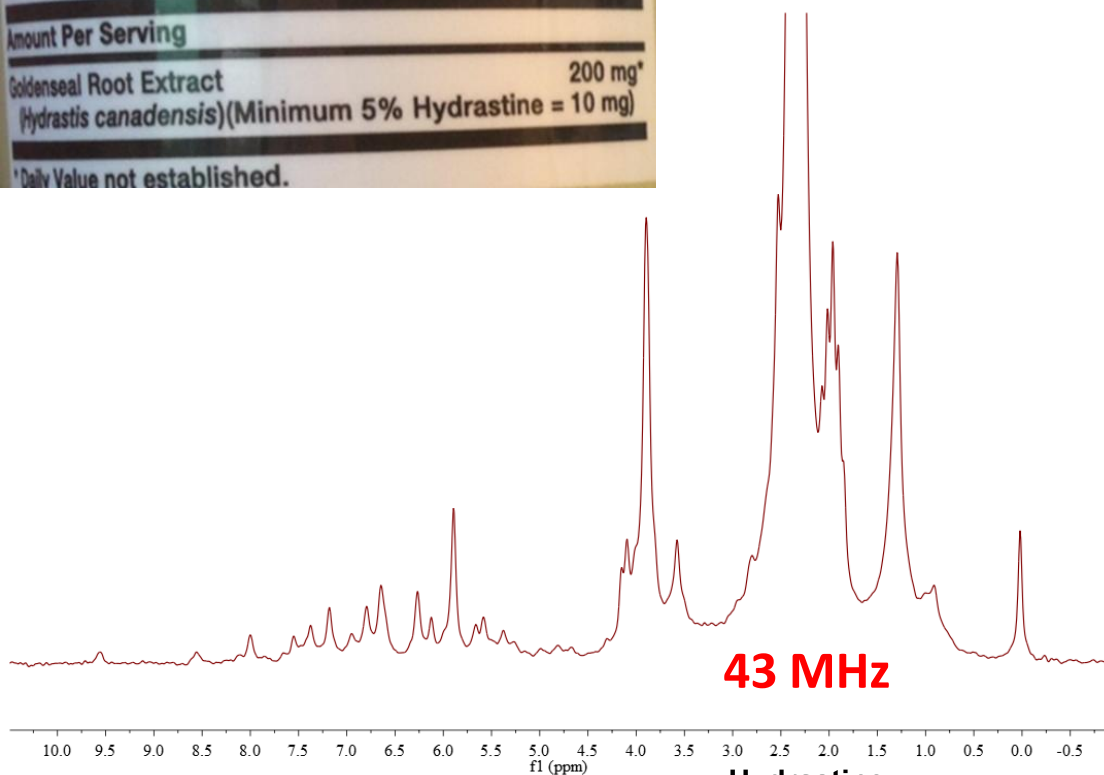
Supplement Facts

Serving Size One Capsule

Amount Per Serving

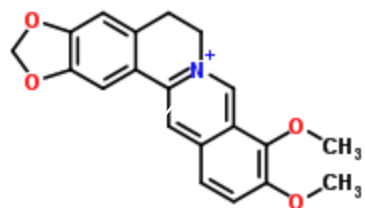
Goldenseal Root Extract 200 mg*
(*Hydrastis canadensis*) (Minimum 5% Hydrastine = 10 mg)

* Daily Value not established.

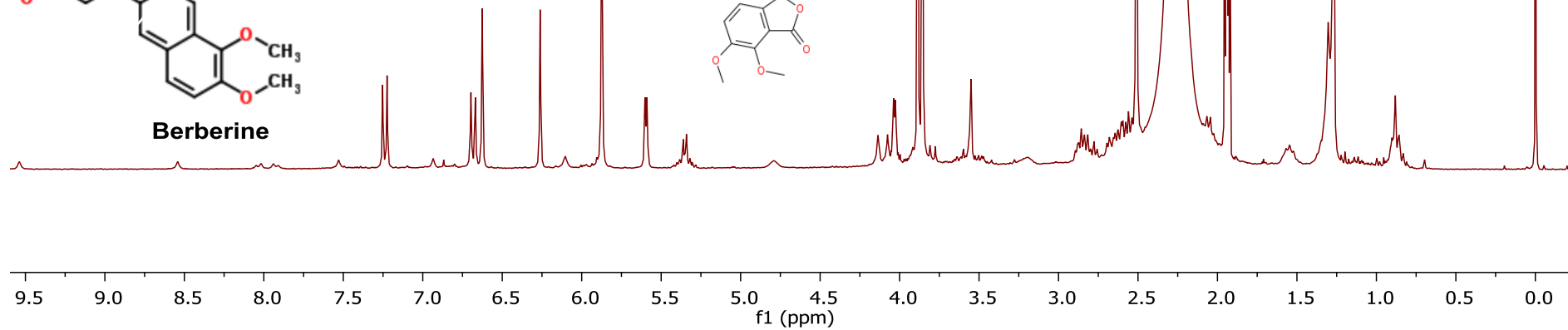
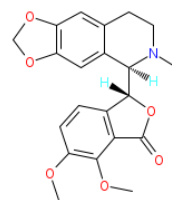


43 MHz

Hydrastine

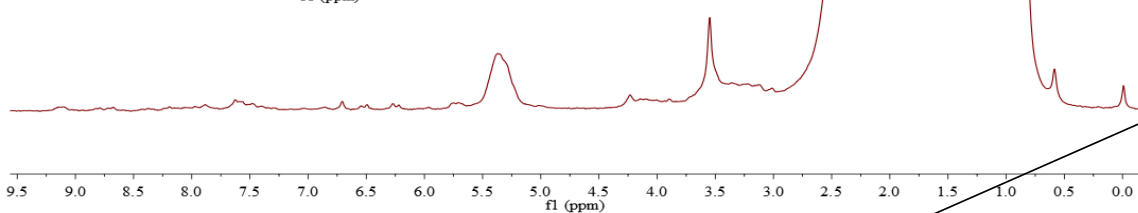
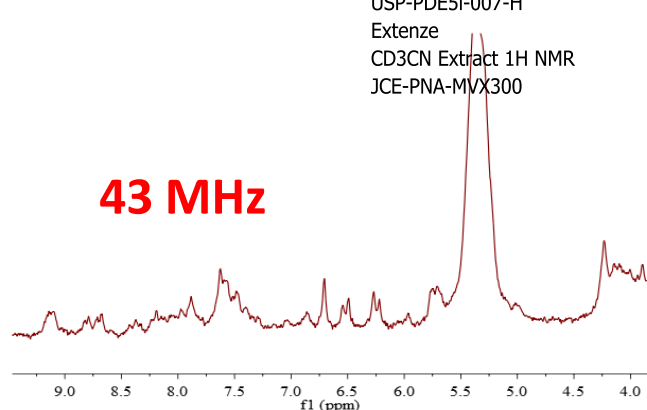


Berberine



USP-PDE5i-007-H
USP-PDE5i-007-H
Extenze
CD3CN Extract 1H NMR
JCE-PNA-MVX300

43 MHz



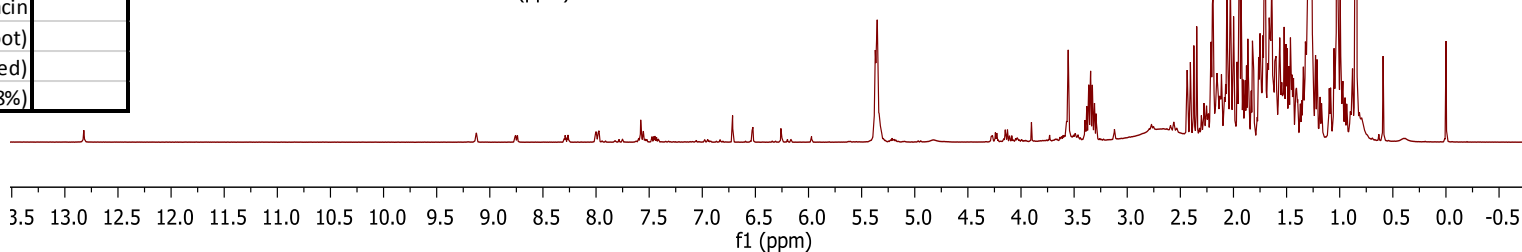
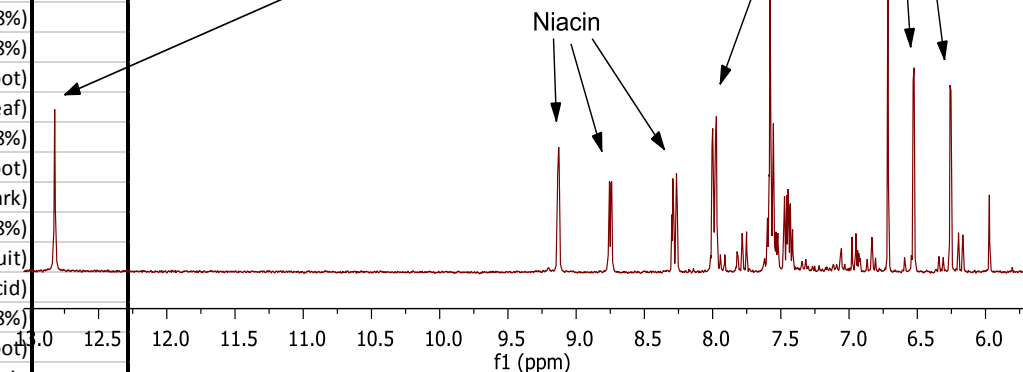
Dehydroepiandrosterone DHEA



Extenze Sexual Response Enhancement	223 mg
Black Pepper extract (fruit)	
Cnidium Extract (seed)	
Damiana Extract (leaf)	
DHEA (98%)	
Gamma-Aminobutyric Acid (GABA-98%)	
Korean Ginseng (root)	
Barrenwort Extract (leaf)	
L-Arginine HCl (98%)	
Licorice Extract (root)	
Muira Puama Extract (bark)	
Pregnenolone (98%)	
Tribulus Extract (fruit)	
Folate (Folic Acid)	
Yohimbe HCl (98%)	
Astragalus Extract (root)	
Niacin	
Tongat Ali Extract (root)	
Velvet Bean Extract (seed)	
Chrysin (98%)	

Niacin

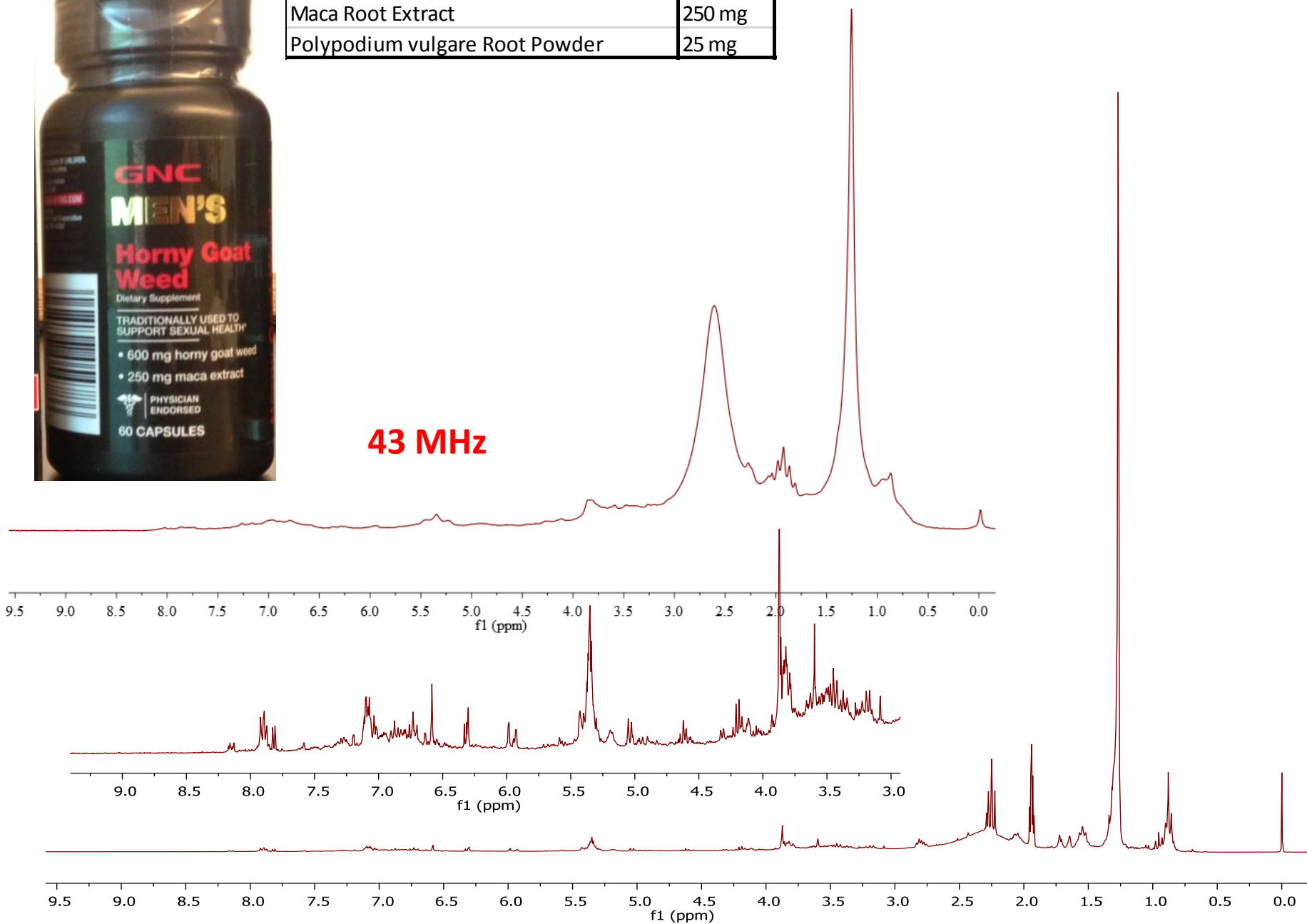
Chrysin

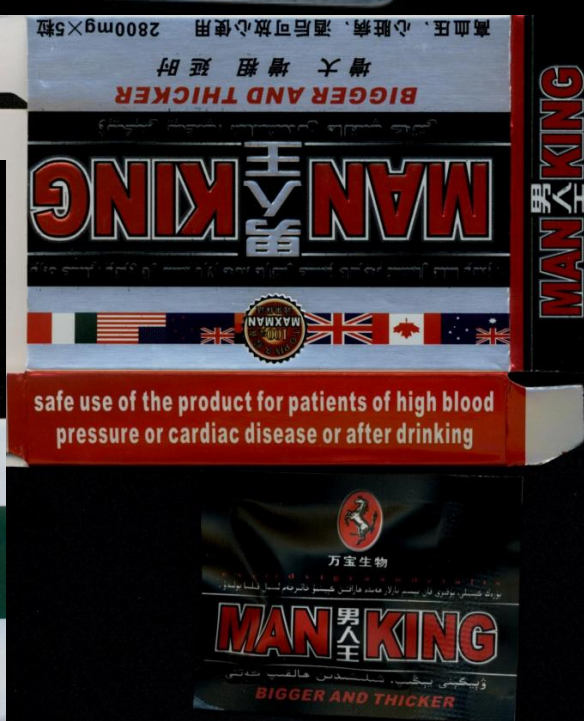


Horny Goat Weed Extract	600 mg
Maca Root Extract	250 mg
Polypodium vulgare Root Powder	25 mg



43 MHz





PDE5-USP-13 - Miracle Zen

43 MHz

Miracle Zen

60 MHz

PDE5i-USP-013
Miracle Zen - CD₃CN Extract
1H NMR in CD₃CN
JCE-PNA-MVX300

300 MHz

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

PDE5i - USP-14 - Shogun X

43 MHz

Shogun X

60 MHz

PDE5i-USP-014
Shogun X - CD₃CN Extract
1H NMR in CD₃CN
JCE-PNA-MVX300

300 MHz

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

PDE5i-USP-16 - Super Power Pills

43 MHz

Super Power Pills

60 MHz

PDE5i-USP-016
Super Power Pills - CD₃CN Extract
1H NMR in CD₃CN
JCE-PNA-MVX300

300 MHz

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

PDE5i-USP-17 - Africa Black Ant

43 MHz

Africa Black Ant

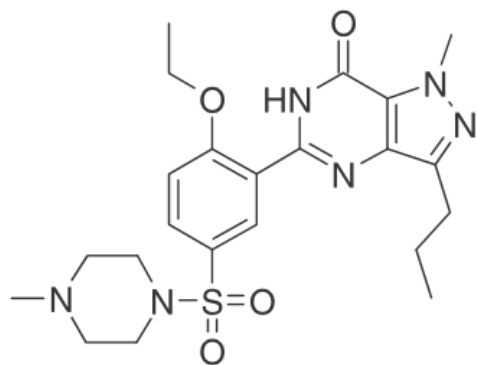
60 MHz

PDE5i-USP-017
Africa Black Ant - CD3CN Extract
1H NMR in CD3CN
JCE-PNA-Merc300

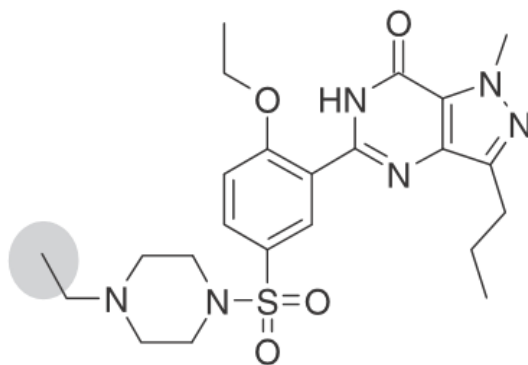
Small amount of Sildenafil
Large amount of Acetomenaphin

300 MHz

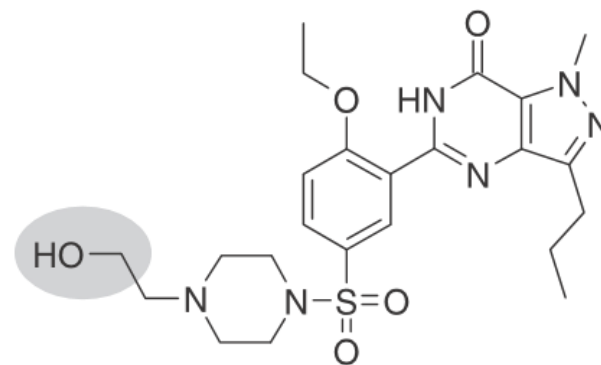
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



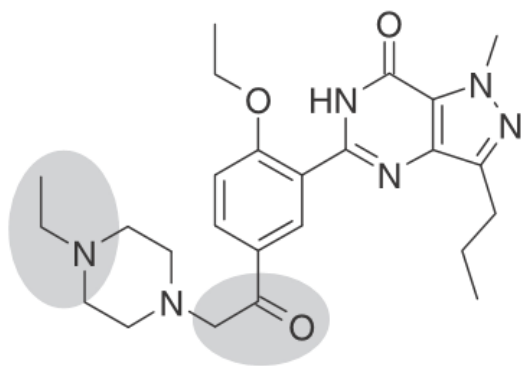
Sildenafil



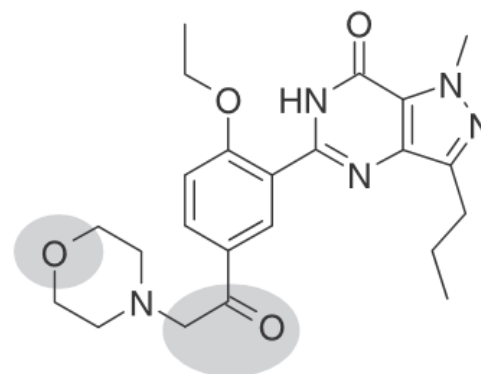
Homosildenafil



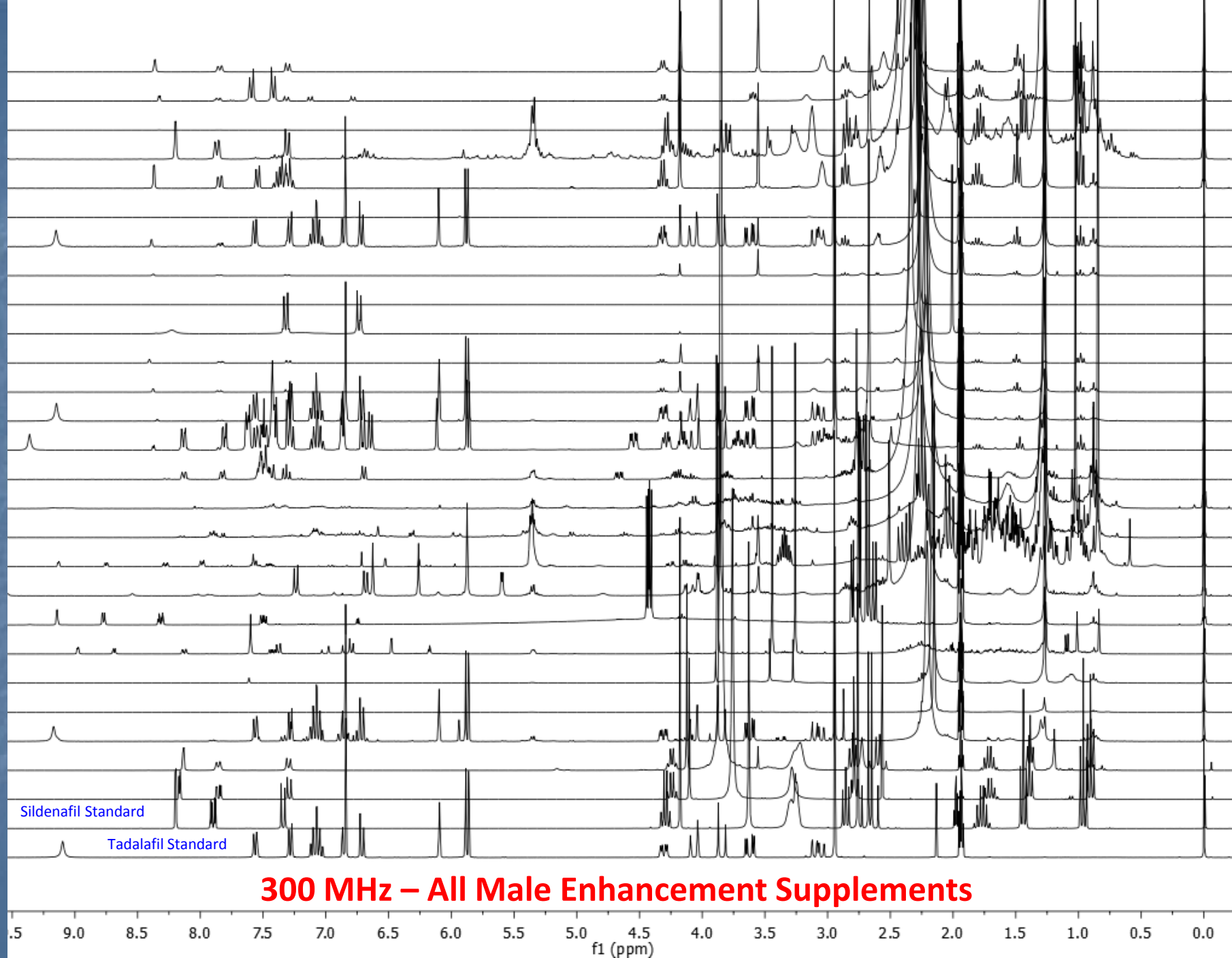
Hydroxy-homosildenafil

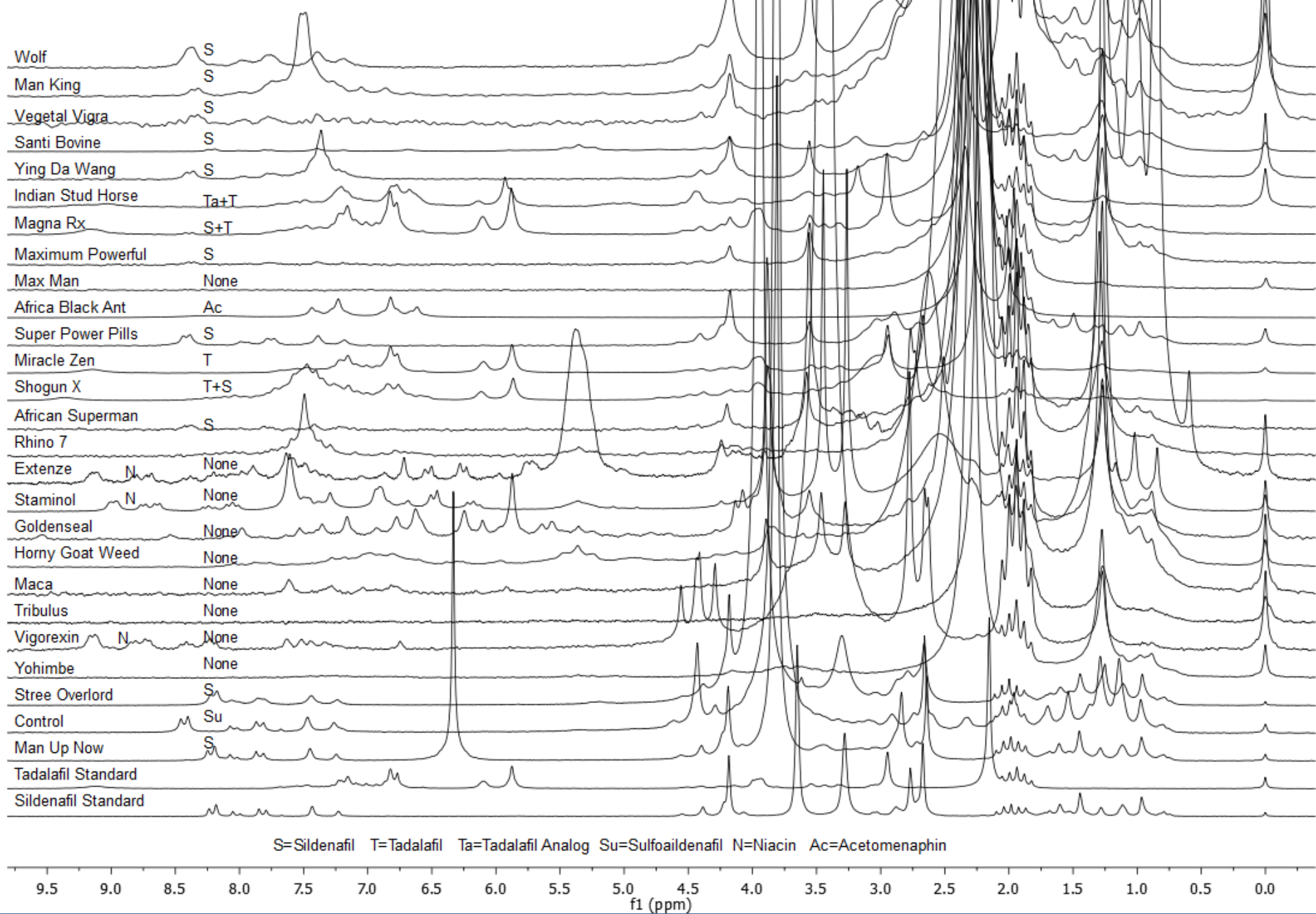


Acetildenafil



Morpholino-acetildenafil





43 MHz – All Male Enhancement Supplements

天然成分能有效阻止食物中的脂肪及過量脂肪身體消化和吸收。服用一段時間後，脂肪積聚部位(如腰、腹、手臂、大腿等)會有明顯改善。其擁有配方結合三種消脂原理：

- ① 降脂——降低卡路里攝取量，能阻擋過量脂肪及轉化為脂肪，從而抑制體內脂肪堆積。
- ② 加速——能將食物中90%的油脂排出體外，減低身體吸收食物中脂肪而達到瘦身的目的。
- ③ 燃燒——能加快新陳代謝，提升細胞率，瞬間燃燒體內積存脂肪，令你24小時不斷在體內自然地燃燒脂肪。

配合達靈運動，能有效地收緊因減肥後出現的鬆弛內，展現肌肉線條
含多種天然草本精華成份，絕不含西藥、防腐劑及重金屬。

成份：薑芝、人參、烏梅、艾實、茯苓、郁李仁、山藥、決明子及麥芽等天然草本精華

建議食法：食三天，每天一次，每次一粒，三天後(如無明顯)，每天一次，每次二粒，早餐前服用較佳，請從少量開始。

忌用者：嚴重疾病者、兒童及孕婦忌服用
儲存方法：避光於陰涼乾燥處或小型不能觸及的地方

日本電氣生產標準認證

BEST SHARE®
Green Coffee
BRAZILIAN SLIMMING COFFEE

18bags

MADE IN USA
Authorized by USA United Chemical Biological Research Institute

男女老幼皆宜
18包裝

Drink Off Pounds
Nothing Could Be Easier

USA

收腰減腹，修腿瘦脸
排毒养颜，均衡营养

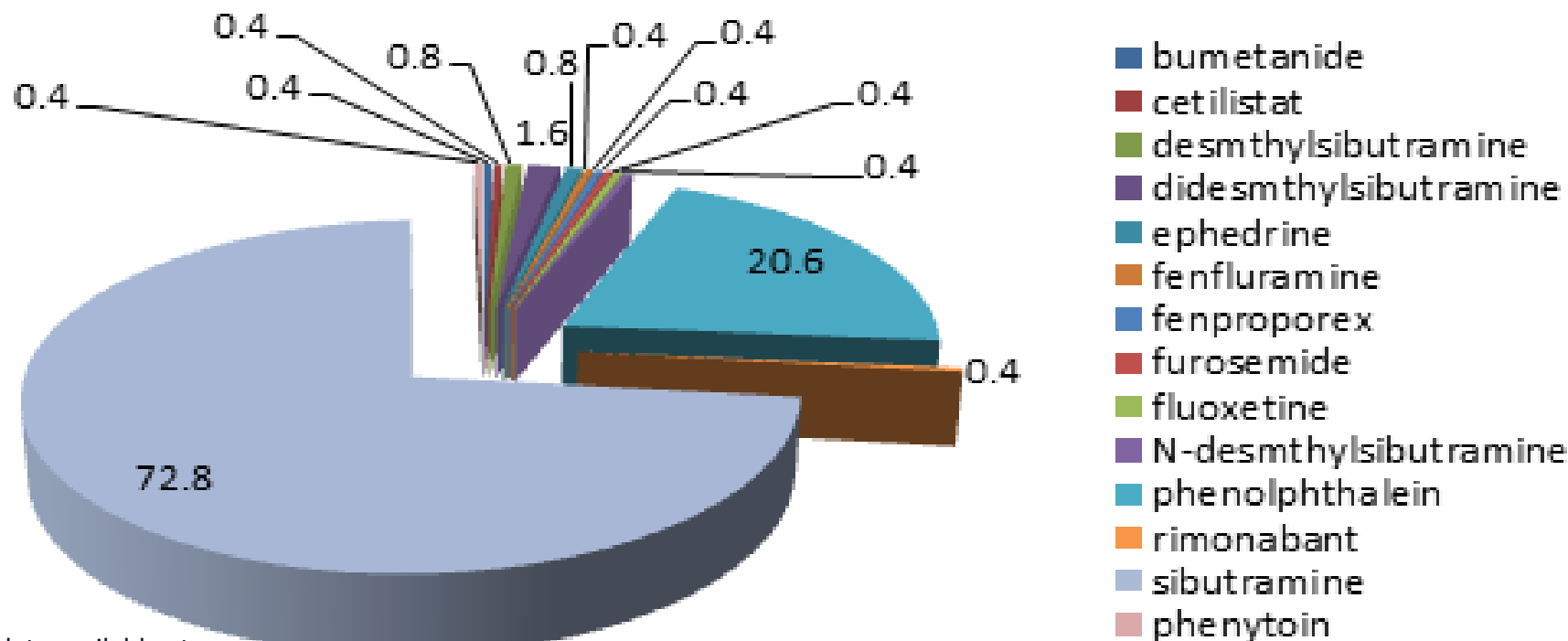
Accept the waist reduces the stomach
to fix the thin face of leg
Line up the poison keeps the balanced
nourishment of

榮獲
美國名牌指定瘦身品牌
2005

達標企業
GMP
衛生監督

·內附俄文說明書·

當日見效
美容瘦身



Based on data available at:
http://www.accessdata.fda.gov/scripts/sda/sdNavigation.cfm?filter=&sortColumn=1d&sd=tainted_supplements_cder&page=1

Table 3 Drug substances identified (in alphabetical order)

Frequently identified	Incidentally identified	
ephedrines	althiazide	phenobarbital
caffeine	amphetamine	phenolphthalein
sibutramine	desmethyilsibutramine	phentermine
synephrine	dexamethazone-21-acetate	phenytoin
	fenfluramine	salicylic acid
	furosemide	spironolacton
	Human Growth Hormone	triamterene
	hydrochlorothiazide	yohimbine

RIVM Report 370030002/2009

Trends in drug substances detected in illegal weight-loss medicines and dietary supplements

A 2002-2007 survey and health risk analysis

Table 4 Combinations of ingredients detected in single products

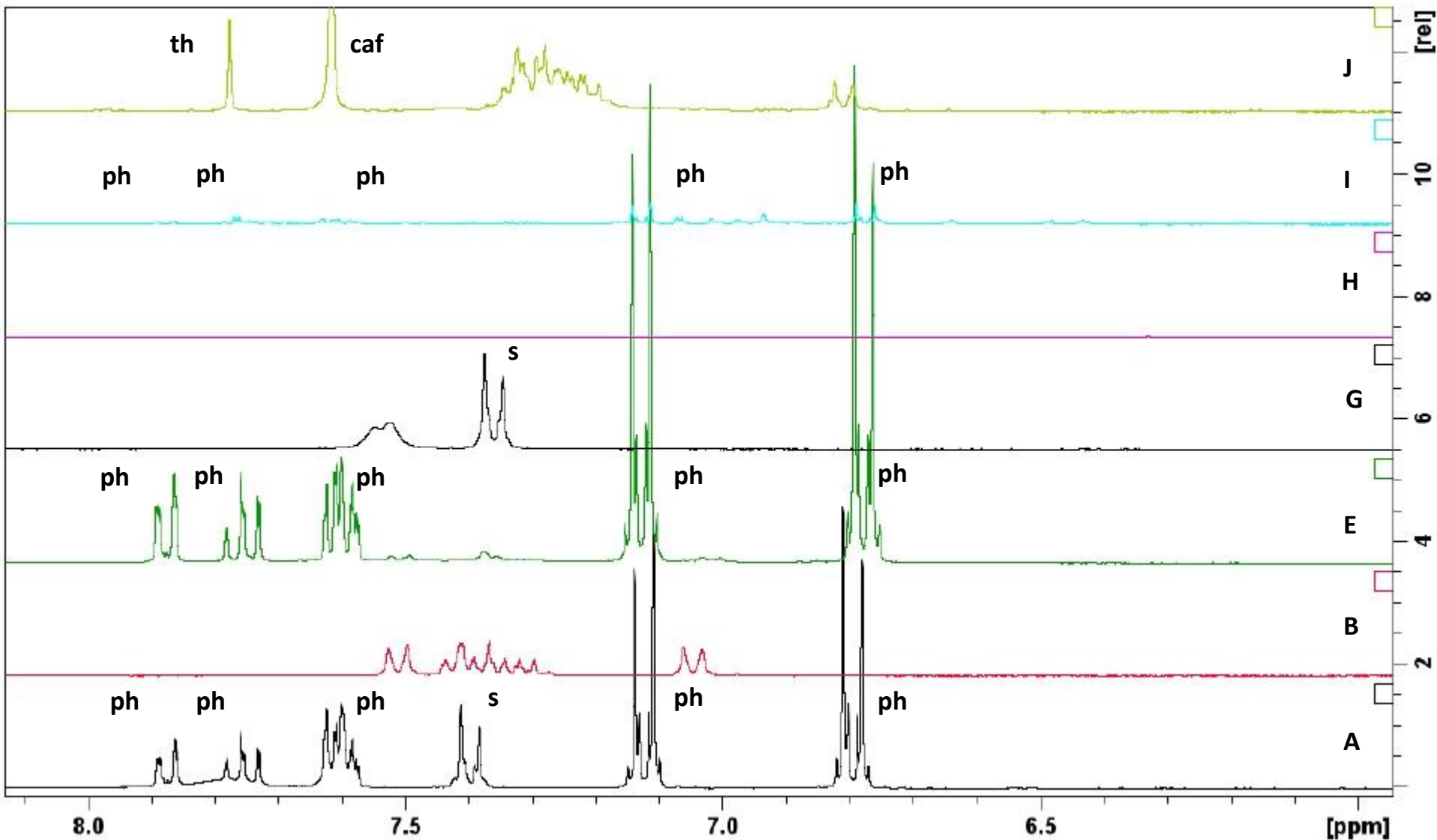
Combinations	
caffeine, ephedrines, synephrine	sibutramine, phenolphthalein
caffeine, ephedrines	phenytoin, phenobarbital, ephedrine
phenylalanine, arginine, pyridoxine, nicotinamide	caffeine, acetylsalicylic acid
pyridoxine, nicotinamide	spironolacton, althiazide

B.J. Venhuis, National Institute for Public Health and the Environment
M.E. Zwaagstra, Customs Laboratory
J.D.J. van den Berg, Netherlands Forensic Institute
H.W.G. Wagenaar, Royal Dutch Association for the Advancement of Pharmacy
A.J.H.P. van Riel, National Poisons Information Center
D.M. Barends, National Institute for Public Health and the Environment
D. de Kaste, National Institute for Public Health and the Environment

A: Meizitang Strong Version (**ph, s**)
B: Fruta Planta (?)
C: Best Share Coffee (**none significant**)
D: Lishou (**none significant**)
E: Pai You Guo (**ph**)

F: Pai You Ji (**no significant**)
G: P57 Hoodia (**s, i?**)
H: Meizitang Botanical Slimming Gelcap (**i?**)
I: 3x Slimming Power (**ph**)
J: Dexaprine XR exp 3/18 (**t, caf**)

s = sibutramine
t = theophylline
caf = caffeine
ph = phenolphthalein



A: Meizitang Strong Version (**ph, s**)

B: Fruta Planta (?)

C: Best Share Coffee (**none significant**)

D: Lishou (**none significant**)

E: Pai You Guo (**ph**)

F: Pai You Ji (**no significant**)

G: P57 Hoodia (**s, i?**)

H: Meizitang Botanical Slimming Gelcap (**i?**)

I: 3x Slimming Power (**ph**)

J: Dexaprine XR exp 3/18 (**t, caf**)

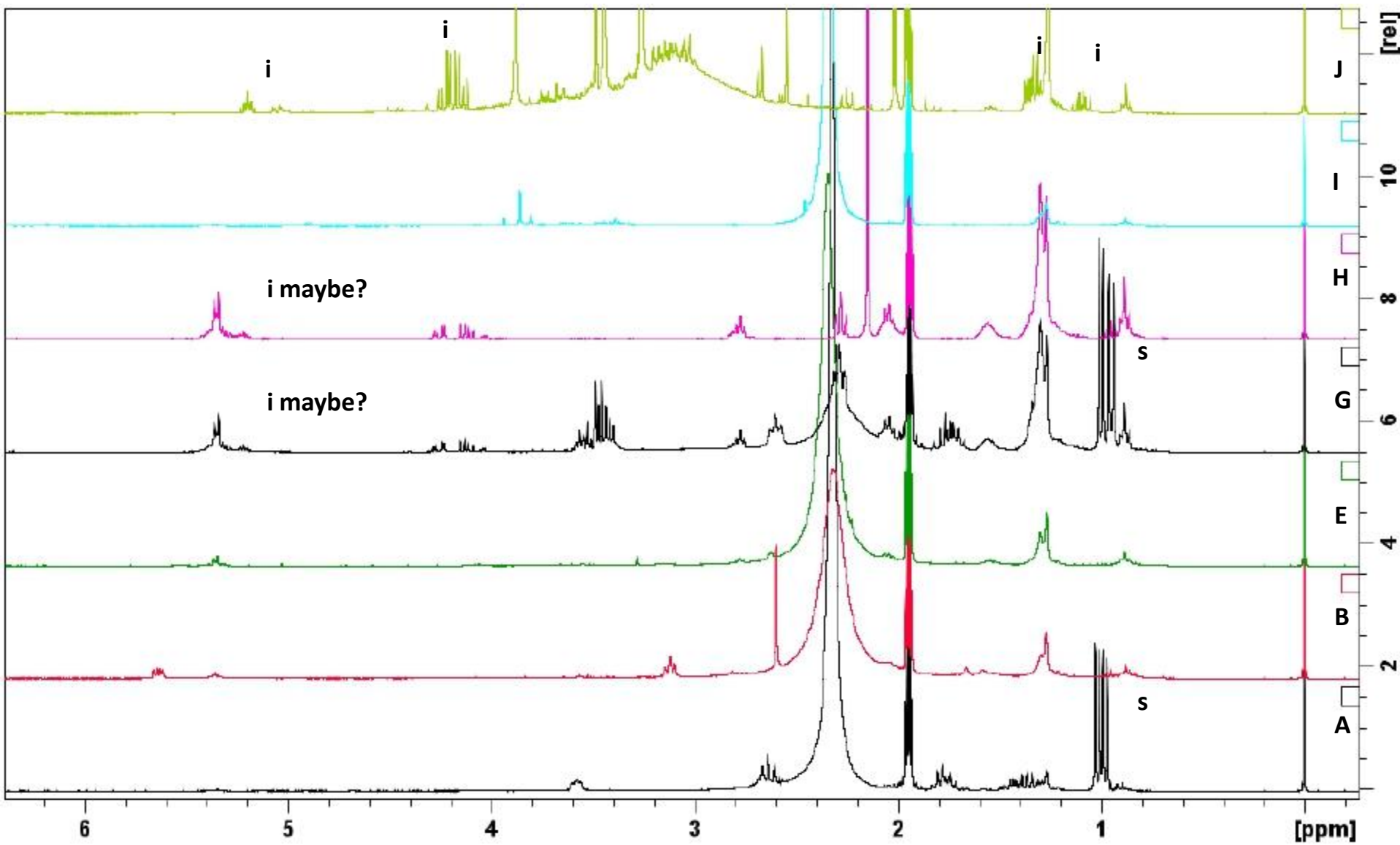
s = sibutramine

t = theophylline

caf = caffeine

ph = phenolphthalein

i = isopropyltopamine



SlimSupp-A Meizitang 280.3mg CD3CN Extract

43 MHz

Slimming Supplement - A

60 MHz

SlimSupp-A
Meizitang
1H NMR CD3CN-D3 Extract
JCE-PNA-MVX300

300 MHz

Phenolphthalein

Sibutramine



10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

SlimSupp-G P57 Hoodia

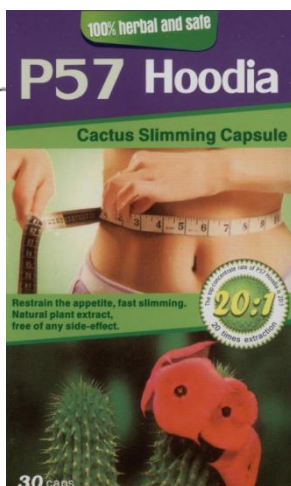
43 MHz

Slimming Supplement G

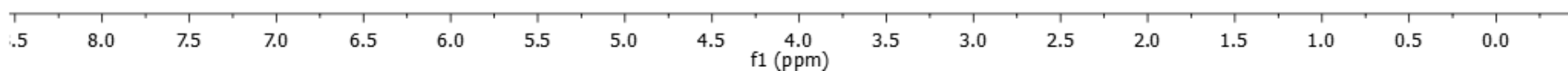
60 MHz

SlimSupp-G
Hoodia P57
1H NMR CD3CN-D3 Extract
JCE-PNA-MVX300

300 MHz



Sibutramine
CH3



SlimSupp-B Fruta Planta 284.9mg CD3CN Extract

43 MHz

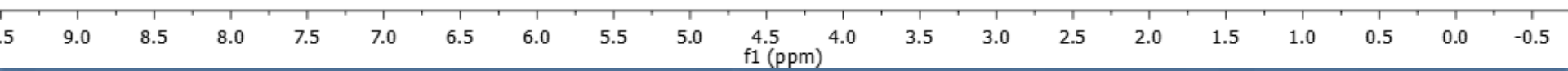
Slimming Supplement B

FDA Warning – 2010 – Contains Sibutramine

60 MHz

SlimSupp-B
Fruta Planta
1H NMR CD3CN-D3 Extract
JCE-PNA-MVX300

300 MHz



SlimSupp-J - Dexaprine XR Exp-3/2018 - CD3CN Extract

A cocktail of synthetic stimulants found in a dietary supplement associated with serious adverse events

Bastiaan Venhuis et al, Drug Testing and Analysis

Volume 6, Issue 6, pages 578–581, June 2014

43 MHz

Caffeine

Slimming Supplement J

UPLC–QTOF-MS: synephrine, oxilofrine, deterenol, yohimbine, caffeine, and theophylline. Two more compounds were found which were tentatively identified as β -methyl- β -phenylethylamines

60 MHz

SlimSupp-J
Dexaprine XR exp 3-2018
1H NMR CD3CN-D3 Extract



8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

Evaluation of a Bench-Top Cryogen-Free Low-Field ^1H NMR Spectrometer for the Analysis of Sexual Enhancement and Weight Loss Dietary Supplements Adulterated with Pharmaceutical Substances

Guilhem Pagès,^{§,†} Anna Gerdova,[‡] David Williamson,[‡] Véronique Gilard,[†] Robert Martino,[†] and Myriam Malet-Martino^{*,†}

[†] Groupe de RMN Biomédicale, Laboratoire de Synthèse et Physicochimie de Molécules d'Intérêt Biologique UMR CNRS 5068, Université de Toulouse, 118 route de Narbonne, 31062 Toulouse cedex 9, France

[‡] Oxford Instruments Industrial Analysis, Tubney Woods, Abingdon, Oxford, UK

Accepted Manuscript

Title: Detection, identification and quantification by ^1H NMR of adulterants in 150 herbal dietary supplements marketed for improving sexual performance

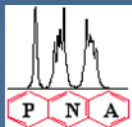
Author: Véronique Gilard Stéphane Balayssac Aurélie Tinaugus Nathalie Martins Robert Martino Myriam Malet-Martino

PII: S0731-7085(14)00502-0
DOI: <http://dx.doi.org/doi:10.1016/j.jpba.2014.10.011>
Reference: PBA 9762

To appear in: *Journal of Pharmaceutical and Biomedical Analysis*

Received date: 17-8-2014
Revised date: 8-10-2014
Accepted date: 10-10-2014





Future Work

Obtain NMR Data on More Standards

Develop ^1H NMR Database at 200-400 and 43-80 MHz

Analysis of 5mg of Sildenafil and Tadalafil Analogs

Investigate More Suspect Supplements

Investigate Use of Different NMR Solvents – DMSO, $\text{CD}_3\text{CN}:\text{D}_2\text{O}$

Develop Automated Analysis Approach ??

Develop AOAC Method Based on NMR

Acknowledgments

Kristie Adams and Anton Bzhelyansky – USP

Paul Giammatteo – PNA

Leap Technologies (43 MHz) - Cosa-Xentaur (60 MHz)