

**Analytical and Bioanalytical Chemistry**

**Electronic Supplementary Material**

**Identification strategy for unknown pollutants using high-resolution mass spectrometry:**

**Androgen-disrupting compounds identified through effect-directed analysis**

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**Table S1.** Information regarding the 59 accurate masses of interest and the corresponding tentatively identified compounds (which fraction the compound was tentatively identified in, theoretical molecular mass (atomic mass units [u], derived from measured mass [M+H] minus one hydrogen), structure name, CAS number, whether or not it was retention time and bioassay confirmed and information found on the internet). Purchased and tested compounds have been attributed a CAS number in bold.

Fraction	Molecular mass (u)	Structure name	CAS number	Retention time confirmed	Bioassay confirmed	Information found at a quick internet search
RP2NP6	313.1356	1,2,4-Triazino[5,6-b]indole, 3-(2-(1-piperidyl)ethylthio)-	212246-31-6	Not purchased		No Google hit
RP2NP6	260.0832	2,5-Diphenylbenzoquinone	844-51-9	Not ionizable		Some Google hits
RP2NP6	363.1288	13-(2,2,2-Trifluoroacetyl)-5,6-benzo-1,4,7,10-tetraoxa-13-azacyclopentadec-5-ene	216099-71-7	Not purchased		No Google hit
RP2NP6	335.0974	N-Naphthalen-2-yl-2-(2-oxo-2-phenylethylsulfanyl)-acetamide	300808-97-3	Not purchased		No Google hit
RP2NP6	339.1465	Papaverin	58-74-2	Wrong retention time		An opium alkaloid used primarily in the treatment of visceral spasm, vasospasm (especially those involving the heart and the brain), and occasionally in the treatment of erectile dysfunction
RP2NP6	265.1461	Desmethyldoxepin	1225-56-5	Not purchased		Desmethyldoxepin is the major metabolite of doxepin. Doxepin is a tricyclic antidepressant that is widely prescribed for the treatment of mild depression
RP2NP7	321.1723	cis-Norlobelanin	6035-31-0	Not purchased		Some Google hits
RP2NP7	234.0134	4-(Trifluoromethyl)phthalic acid	835-58-5	Not purchased		Suppliers and patent hits
RP2NP7	340.0703	4-Naphtho[2,3-d][1,2,3]triazol-1-yl-5-nitro-phthalonitrile	no	Not purchased		No Google hit
RP2NP7	231.2193	1,1-bis(2,2-dimethylpropoxy)-N,N-dimethyl-Methanamine	4909-78-8	Not purchased		No Google hit
RP2NP7	162.0675	p-Methoxycinnamaldehyde	1963-36-6	Wrong retention time		Exists in the Pesticide database and is a flavoring agent
		Methyl cinnamate	103-26-4	Wrong retention time		Flavoring and fragrance agent (strawberry and cinnamon)
		Cinnamyl formate/Cinnamyl methanoate	104-65-4	Not ionizable		Flavoring agent

		Izosafrol	120-58-1	Wrong retention time		Isosafrole is an aromatic organic chemical with a smell similar to anise or licorice. It is found in small amounts in various essential oils, but is most commonly obtained by isomerizing the plant oil safrole.
		Safrene/Safrol/Shikimole/Rhyuno oil	94-59-7	Not ionizable		Safrole is a colorless or slightly yellow oily liquid. It is typically extracted from the root-bark or the fruit of sassafras plants in the form of sassafras oil, or synthesized from other related methylenedioxy compounds. It is the principal component of brown camphor oil, and is found in small amounts in a wide variety of plants, where it functions as a natural pesticide. Safrole is often used as the precursor for the clandestine manufacture of MDMA (ecstasy).
		trans-Methyl Cinnamate	1754-62-7	Not purchased		Flavoring agent (bourbon vanilla)
RP2NP7	250.0445	Di(1,2,5-oxadiazolo)[3,4-b;3,4-E]pyrazine, 4,8-diacetyl-	186205-18-5	Not purchased		Only supplier at Google
RP2NP7	248.1407	Parthenolide	20554-84-1	Wrong retention time		Sesquiterpene lactones common in natural medicines
		Confertin	19908-69-1	Not purchased		Sesquiterpene lactones common in natural medicines
		Tomentosin/Parthenium	33649-15-9	Not purchased		Sesquiterpene lactones common in natural medicines
RP2NP7	217.0886	Benzo(a,b or c)carbazole	239-01-0	Not purchased		Benzo(b)carbazole exists in coal tar
RP2NP7	360.2659	6à-Pentyl-4-oxa-5á-androstane-3,17-dione	59251-71-7	Not purchased		No Google hit
RP2NP7	232.1458	Isovelleral	37841-91-1	Not purchased		Some kind of a natural product Sesquidecade
		Isoalantolactone	470-17-7	Not purchased		Some kind of a natural product Sesquidecade
RP2NP7	274.1927	Nandrolone	434-22-0	Correct retention time	Confirmed androgen	Anabolic steroid
RP2NP7	220.1458	Ibuprofen methyl derivative	61566-34-5	Not purchased		Degradation product of ibuprofen
RP2NP7	203.0729	4-Azapyrene	194-03-6	Not purchased		Polyaromatic hydrocarbon
RP2NP7	272.1771	19-Norandrostenedione	734-32-7	Not purchased		Anabolic steroids banned in 2007
RP2NP7	228.0603	Benzeneethanethioic acid, S-phenyl ester	18245-74-4	Not purchased		Some Google hits

RP2NP7	256.0916	3-Phenylthiopropionic acid, S-benzyl ester	133535-77-0	Not purchased		No Google hit
RP2NP7	326.0002	Tris(2-chloroisopropyl)phosphate	13674-84-5	Correct retention time	Confirmed anti-androgen	Organophosphorus flame retardant and pesticide
RP3NP2	289.2068	4-(t-butyl(dimethylsilyloxy)-3-nitro-2-methylheptane	344351-74-2	Not purchased		No Google hit
RP3NP2	289.1672	1-[5-(1,3-benzodioxol-5-yl)-1-oxopentyl]-piperidine	23434-88-0	Not purchased		US Patent 6849645 - Method of increased bioavailability of nutrients and pharmaceutical preparations with tetrahydropiperine and its analogues and derivatives
RP3NP5	308.1166	(5-Bromo-1,2-dimethyl-pentylloxy)-t-butyl-dimethyl-silane	no	Not purchased		Only supplier at Google
RP3NP5	272.1559	Benzene, 1,1',1''-(1-propanyl-3-ylidene)tris-	19120-39-9	Not purchased		Some Google hits
RP3NP5	244.1822	Celestolide	13171-00-1	Wrong retention time		Musk, fragrance
		Phantolid	15323-35-0	Wrong retention time		Musk, fragrance
RP3NP5	270.1978	Androstadienone	1912-63-6	Not purchased		Sexual pheromones (male sweat). Identified in sewage treatment works effluent to be one of the responsible androgens in the EDA (Thomas et al., 2002)
			32222-21-2	Not purchased		
			4075-07-4	Not purchased		
RP3NP5	256.1822	Deoxyestradiol	2529-64-8	Not purchased		Steroids
			53-63-4	Not purchased		
RP3NP5	289.2400	Androstanones oxime	54156-19-3	Not purchased		Sexual pheromones
			17556-10-4	Not purchased		
			54156-20-6	Not purchased		
			14614-11-0	Not purchased		
			14546-37-3	Not purchased		
			14475-43-5	Not purchased		

			54156-21-7	Not purchased		
			54156-18-2	Not purchased		
			1035-62-7	Not purchased		
RP3NP5	266.1615	Monododecyl phosphate	2627-35-2	Not purchased		Organophosphorus flame retardant
		Tributyl phosphate	126-73-8	Correct retention time	No activity	Organophosphorus flame retardant
RP3NP5	240.1509	Benzylidenecamphor	15087-24-8	Not purchased		Industrial chemical
RP3NP5	258.1978	Musk 36A	88-29-9	Not purchased		Musk, fragrance
		Tonalide	1506-02-1	Correct retention time	Confirmed anti-androgen	Musk, fragrance
		Galoxolide	1222-05-5	Correct retention time	Confirmed anti-androgen	Musk, fragrance
		Traseolide	68140-48-7	Correct retention time	Confirmed anti-androgen	Musk, fragrance
RP3NP5	280.1798	Methyl bis(1,2,2-trimethylpropyl) phosphate	108202-69-3	Not purchased		Organophosphorus flame retardant
RP3NP5	268.1822	2-tert-Butyl-6-(1-methyl-1-phenylethyl)phenol	17959-04-5	Not purchased		Possible other isomers of the structure
RP3NP5	390.1969	Perhydrobenzo[e]isoxazolo[2,3-b][1,2]oxazine-3-carboxamide,4-phenyl-8a-[(1,1,1-trimethylsilyl)oxy]	no	Not purchased		No Google hit
RP3NP5	290.1822	Diphenyl-(1,2,3-trimethylcyclopent-2-enyl)methanol	no	Not purchased		No Google hit
RP3NP5	272.2135	Androstenone	4354-37-4	Not purchased		Sexual pheromones
			25824-61-7	Not purchased		
			18339-16-7	Correct retention time	Confirmed strong anti-androgen and weak androgen	
			25824-80-0	Not purchased		

			3248-10-0	Not purchased		
			13583-72-7	Not purchased		
			54548-20-8	Not purchased		
			2872-90-4	Not purchased		
			963-75-7	Not purchased		
RP3NP5	282.1978	Methylated androstatrienone	77702-25-1	Not purchased		Sexual pheromones
		Methylated androstadienone	111660-89-0	Not purchased		
RP3NP5	284.2135	Dehydroabietal	13601-88-2	Not purchased		Present in bark and marihuana
RP3NP5	388.2608	Dehydrodeoxycholic acid	2958-05-6	Not purchased		Bile acid
RP3NP6	314.1656	Fumarylacetone diethoxime mono-TMS	no	Not purchased		Not likely this derivative compound would be present
RP3NP6	270.1396	Methylated thiopental	80783-03-5	Not purchased		Google search on thiopental gave: "...is a rapid-onset short-acting barbiturate general anaesthetic".
RP3NP6	230.0726	7H-Benz[de]anthracen-7-one	82-05-3	Correct retention time	Confirmed anti-androgen	Benzanthrone is an aromatic hydrocarbon derivate used as a dyestuff intermediate for anthraquinone-based dyes.
		1-Pyrene-carboxaldehyde	3029-19-4	Wrong retention time		Some Google hits
RP3NP7	389.2924	17-Acetoxyandrostane, 5,19-(1-oxa-4-azabutanediyl)-, N-methyl-	no	Not purchased		No Google hit
RP3NP7	375.1396	Haloperidol	52-86-8	Wrong retention time		Antipsychotic
RP3NP7	366.2189	Bis[3,3,4,7-tetramethyl-1,3-2H-benzofuran-1-yl] ether	146950-82-5	Not purchased		No Google hit
		Drospirenone	67392-87-4	Not purchased		From PubChem search results only. Not in NIST. Antiandrogenic potent synthetic progestin.
RP3NP7	360.2659	Drolban	521-12-0	Not purchased		Anabolic steroid
RP3NP7	253.0884	N,N-Diethyl-2,3,4,5,6-pentafluorobenzylamine	54496-01-4	Not purchased		No Google hit
RP3NP7	250.0980	Triazene, 1-tert-butyl-1-cyanomethyl-3-(m-chlorophenyl)-	no	Not purchased		Only supplier at Google

RP3NP7	242.0760	3-Phenylthiopropionic acid, S-phenyl ester	53573-33-4	Not purchased		Some Google hits
RP4NP2	290.2029	9,10-Dibutylanthracene	1624-34-6	Not purchased		Some Google hits
RP4NP7	373.3703	6-Azacholestane	16359-52-7	Not purchased		Some Google hits
RP4NP7	434.3519	Phosphoric acid, tris(2-ethylhexyl) ester	78-42-2	Correct retention time	Confirmed anti-androgen	Organophosphorus flame retardant
RP4NP7	344.3285	Batilol	544-62-7	Wrong retention time		The drug stimulates erythrocytes and leukocytes. It stops the flow of blood and hemoglobin in radiation effects on the body and helps speed up their recovery.
RP4NP7	358.2866	1.3-Hydroxychole-9(11)-en-12-one	42921-48-2	Not purchased		No Google hit
RP4NP7	259.2294	1,1'-Bis(bicyclo [2.2.1] hept-5-yl) ethyl ethenylamine	no	Not purchased		No Google hit
RP4NP7	374.2815	Tetrahydropyran Z-10-dodecenoate	no	Not purchased		No Google hit
		3Beta-hydroxy-5-chole-24-oic acid	5255-17-4	Not purchased		Bile acids
		3-Oxocholanic acid	1553-56-6	Not purchased		Bile acids