

**Table S1.** Identified metabolites in urine samples of PCa patients and healthy subjects. Retention time (RT) in min, formula, CAS number and chemical family is reported for each compound. Frequency of occurrence as a percentage (%) and mean relative peak areas are reported for prostate cancer and control groups ( $n = 3$ ; RSD < 20 %).

RT (min)	VOM	Formula	CAS No.	Chemical family	Frequency of occurrence (%)		Mean relative peak area	
					PCa	CTRL	PCa	CTRL
20.13	6-Methylphenanthridine	C <sub>14</sub> H <sub>11</sub> N	3955-65-5	HHc	81	100	4.38	10.50
20.77	2-Pentanone	C <sub>5</sub> H <sub>10</sub> O	107-87-9	Ket	54	57	3.65	5.70
22.30	3-Nonyne	C <sub>9</sub> H <sub>16</sub>	20184-89-8	Hc	4	3	0.24	0.09
22.93	1-Methylcycloheptene	C <sub>8</sub> H <sub>14</sub>	55308-20-8	Hc	19	10	1.22	0.92
23.37	(+)-Linalool	C <sub>10</sub> H <sub>18</sub>	10281-56-8	Ter	4	0	0.26	-
23.61	1,3-Dimethyl-1-cyclohexene	C <sub>8</sub> H <sub>14</sub>	2808-76-6	Hc	50	37	3.09	3.04
23.90	1-Decene	C <sub>10</sub> H <sub>20</sub>	872-05-9	Hc	4	0	0.17	-
24.41	3-Hexanone	C <sub>6</sub> H <sub>12</sub> O	589-38-8	Ket	19	13	0.66	0.39
25.23	<i>p</i> -Menth-3-ene	C <sub>10</sub> H <sub>18</sub>	500-00-5	Ter	4	7	0.80	0.30
26.14	Dimethyl disulfide	C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>	624-92-0	SC	100	100	20.01	20.88
26.39	Hexanal	C <sub>6</sub> H <sub>12</sub> O	66-25-1	Ald	19	20	1.92	1.36
28.64	4-Heptanone	C <sub>7</sub> H <sub>14</sub> O	123-19-3	Ket	100	100	30.76	37.48
29.85	<i>o</i> -Xylene	C <sub>8</sub> H <sub>10</sub>	95-47-6	BD	4	3	0.14	0.10
31.89	1,4-Cineol	C <sub>10</sub> H <sub>18</sub> O	470-67-7	Ter	4	13	0.24	0.57
31.96	2-Carene	C <sub>10</sub> H <sub>16</sub>	554-61-0	Ter	4	20	0.15	2.23
32.06	$\alpha$ -Terpinene	C <sub>10</sub> H <sub>16</sub>	99-86-5	Ter	19	23	1.23	2.00
32.58	2-Heptanone	C <sub>7</sub> H <sub>14</sub> O	110-43-0	Ket	4	0	0.14	-
33.86	4-Methyl-2-heptanone	C <sub>8</sub> H <sub>16</sub> O	6137-06-0	Ket	8	0	0.15	-
33.99	Eucalyptol	C <sub>10</sub> H <sub>18</sub> O	470-82-6	Ter	4	10	0.10	1.09
34.70	1-Pentylcyclohexene	C <sub>11</sub> H <sub>20</sub>	15232-85-6	Hc	0	7	-	0.84
35.68	2,2-dimethyl-5-(1-methyl-1-propenyl)-tetrahydrofuran	C <sub>10</sub> H <sub>18</sub> O	7416-35-5	FC	96	83	10.01	11.90
36.18	$\gamma$ -Terpinene	C <sub>10</sub> H <sub>16</sub>	99-85-4	Ter	15	20	0.36	1.32
37.04	3,5-Dihydroxybenzamide	C <sub>7</sub> H <sub>7</sub> NO <sub>3</sub>	3147-62-4	BD	15	3	1.27	0.08
37.09	3,4-Dimethylthiophene	C <sub>6</sub> H <sub>8</sub> S	632-15-5	SC	4	10	0.08	0.42

37.59	<i>p</i> -Cymene	C <sub>10</sub> H <sub>14</sub>	99-87-6	Ter	81	33	12.52	14.86
37.85	<i>o</i> -Cymene	C <sub>10</sub> H <sub>14</sub>	527-84-4	Ter	58	67	4.91	25.73
38.54	$\alpha$ -Terpinene	C <sub>10</sub> H <sub>16</sub>	99-86-5	Ter	15	7	1.97	0.74
38.62	<i>m</i> -Cymene	C <sub>10</sub> H <sub>14</sub>	535-77-3	Ter	4	3	0.06	0.06
38.79	Allyl methyl disulfide	C <sub>4</sub> H <sub>8</sub> S <sub>2</sub>	2179-58-0	SC	8	17	0.86	1.32
39.05	Isoterpinolene	C <sub>10</sub> H <sub>16</sub>	586-63-0	Ter	35	3	1.37	0.69
40.13	1,4,6-Trimethylnaphthalene	C <sub>13</sub> H <sub>14</sub>	2131-42-2	Nor	8	0	0.85	-
40.41	1,6,7-Trimethylnaphthalene	C <sub>13</sub> H <sub>14</sub>	2245-38-7	Nor	4	10	0.32	0.55
40.88	2,6-Dimethyl-1,6-octadiene	C <sub>10</sub> H <sub>18</sub>	80-49-35	Hc	4	0	0.28	-
40.97	1,3-Cycloheptadiene	C <sub>7</sub> H <sub>10</sub>	4054-38-0	Hc	12	3	0.87	0.12
40.97	2,3,6-Trimethylnaphthalene	C <sub>13</sub> H <sub>14</sub>	829-26-5	Nor	4	0	0.23	-
40.98	2,2,6-Trimethylcyclohexanone	C <sub>9</sub> H <sub>16</sub> O	2408-37-9	Ket	4	10	0.14	0.28
41.97	Hemimellitene	C <sub>9</sub> H <sub>12</sub>	526-73-8	BD	15	3	0.95	0.26
42.10	<i>p</i> -Ethyltoluene	C <sub>9</sub> H <sub>12</sub>	622-96-8	BD	8	20	0.85	2.10
43.15	<i>p</i> -Methylstyrene	C <sub>9</sub> H <sub>10</sub>	622-97-9	BD	4	7	0.05	0.23
44.37	2-Methoxy-5-methylthiophene	C <sub>6</sub> H <sub>8</sub> OS	31053-55-1	SC	46	13	4.29	1.13
44.47	2-Methyl-5-(methylthio)furan	C <sub>6</sub> H <sub>8</sub> OS	13678-59-6	FC	42	73	5.32	6.12
44.58	Nonanal	C <sub>9</sub> H <sub>18</sub> O	124-19-6	Ald	12	0	1.73	-
44.95	Dimethyl trisulfide	C <sub>2</sub> H <sub>6</sub> S <sub>3</sub>	3658-80-8	SC	46	17	2.79	1.23
45.19	2-Carene	C <sub>10</sub> H <sub>16</sub>	554-61-0	Ter	0	3	-	0.12
45.21	Allo-Ocimene	C <sub>10</sub> H <sub>16</sub>	673-84-7	Ter	0	7	-	0.28
46.09	Tetrahydrideinalool	C <sub>10</sub> H <sub>22</sub> O	57706-88-4	Ter	19	20	1.90	3.84
46.36	<i>m</i> -Di-tert-butylbenzene	C <sub>14</sub> H <sub>22</sub>	1014-60-4	BD	0	3	-	0.27
46.88	1,5,7-trimethyl-1,2,3,4-tetrahydronaphthalene	C <sub>13</sub> H <sub>18</sub>	21693-55-0	Nor	0	3	-	0.37
47.33	<i>p</i> -Cymenene	C <sub>10</sub> H <sub>12</sub>	1195-32-0	Ter	96	97	19.08	39.30
47.64	<i>o</i> -Cymenene	C <sub>10</sub> H <sub>12</sub>	7399-49-7	Ter	0	10	-	0.66
47.69	3-Methyl-2-butenic acid, tridec-2-ynyl ester	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	100029-93-1	Est	4	0	0.53	0.00
48.04	Dihydromyrcenol	C <sub>10</sub> H <sub>20</sub> O	18479-58-8	Ter	96	83	17.57	11.58
48.11	$\alpha$ -Ionene	C <sub>13</sub> H <sub>18</sub>	30316-36-0	Nor	0	7	-	1.11

48.95	<i>t</i> -Furan linalool oxide	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>	34995-77-2	FC	46	57	2.31	6.72
49.05	Nerol oxide	C <sub>10</sub> H <sub>16</sub> O	1786-08-9	Ter	4	0	0.78	-
49.23	2-Ethyl-1-hexanol	C <sub>8</sub> H <sub>18</sub> O	104-76-7	Alc	100	100	9.19	8.92
49.42	2-Mercapto-4-phenylthiazole	C <sub>9</sub> H <sub>7</sub> NS <sub>2</sub>	2103-88-0	HHc	12	0	1.65	0.00
50.52	Prehnitene	C <sub>10</sub> H <sub>14</sub>	488-23-3	Ter	58	50	5.29	4.83
51.04	Theaspirane	C <sub>13</sub> H <sub>22</sub> O	36431-72-8	Nor	69	67	3.99	6.30
51.57	Carvestrene	C <sub>10</sub> H <sub>16</sub>	499-03-6	Ter	4	0	0.20	-
52.25	2,5-Diisopropyl-p-xylene	C <sub>14</sub> H <sub>22</sub>	10375-96-9	BD	0	13	-	0.98
52.46	β-Ionone	C <sub>13</sub> H <sub>20</sub> O	6901-97-9	Nor	85	83	22.00	28.77
52.92	Theaspirane	C <sub>13</sub> H <sub>22</sub> O	100019-43-4	No	65	80	3.85	7.31
53.18	2-(Methylthio)thiophene	C <sub>5</sub> H <sub>6</sub> S <sub>2</sub>	5780-36-9	SC	8	0	0.26	-
53.43	Cadalene	C <sub>15</sub> H <sub>18</sub>	483-78-3	Ses	8	10	0.17	0.80
54.10	α-Ionene	C <sub>13</sub> H <sub>18</sub>	475-03-6	Nor	12	27	0.93	1.15
54.70	5-Methylfurfural	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	620-02-0	FC	42	40	4.56	3.83
54.70	2-Fenchanol	C <sub>10</sub> H <sub>18</sub> O	1632-73-1	Ter	8	0	0.20	-
54.84	1-Methylene-spiro[4.4]nonane	C <sub>10</sub> H <sub>16</sub>	19144-06-0	Hc	0	10	-	0.55
55.20	(±)-Neoisomenthol	C <sub>10</sub> H <sub>20</sub> O	491-02-1	Ter	54	57	5.66	4.66
55.79	Terpinene-4-ol	C <sub>10</sub> H <sub>18</sub> O	000562-74-3	Ter	8	7	0.14	1.12
55.98	2-Methyl-benzofuran	C <sub>9</sub> H <sub>8</sub> O	4265-25-2	FC	4	10	0.09	0.39
56.69	2-Ethyl-1-butene	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	620-02-0	Hc	12	13	1.96	0.69
57.26	Menthol	C <sub>10</sub> H <sub>20</sub> O	15356-70-4	Ter	85	97	19.86	25.17
57.86	Myrtenal	C <sub>10</sub> H <sub>14</sub> O	564-94-3	Ter	8	7	0.30	0.21
58.29	6-Methyl-3(2H)-pyridazinone	C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O	13327-27-0	HHc	4	10	0.26	0.33
58.66	1,1,4,7-Tetramethylindan	C <sub>13</sub> H <sub>18</sub>	1078-04-2	Hc	35	43	3.34	3.57
58.76	α-Ionene	C <sub>13</sub> H <sub>18</sub>	475-03-6	Nor	8	10	0.83	0.62
59.66	Durene	C <sub>10</sub> H <sub>14</sub>	95-93-2	Ter	4	17	0.21	1.46
59.86	γ-Vinyl-γ-valerolactone	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	1073-11-6	FC	27	33	1.91	2.80
59.87	2,3,5,5,8,8-Hexamethyl-1,3,6-cyclooctatriene	C <sub>14</sub> H <sub>22</sub>	100016-19-7	Hc	0	0	-	-
59.87	2,5-Diisopropyl-p-xylene	C <sub>14</sub> H <sub>22</sub>	10375-96-9	BD	0	7	-	0.33

60.18	p-Menth-1(7)-en-2-one	C <sub>10</sub> H <sub>16</sub> O	15297-07-1	Ter	15	33	2.20	3.15
60.60	$\alpha$ -Cyclogeraniol	C <sub>10</sub> H <sub>18</sub> O	6627-74-3	Ter	4	0	0.22	-
61.06	1,5,8-Trimethyl-1,2,3,4-tetrahydronaphthalene	C <sub>13</sub> H <sub>18</sub>	21693-51-6	Nor	4	13	0.96	1.05
61.37	$\alpha$ -Methyl-cinnamaldehyde	C <sub>10</sub> H <sub>14</sub> O	585-34-2	Ald	8	53	0.40	5.53
61.42	4,7-Dimethylbenzofuran	C <sub>10</sub> H <sub>10</sub> O	28715-26-6	FC	27	43	1.45	6.14
61.49	1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene	C <sub>13</sub> H <sub>18</sub>	30316-36-0	Nor	12	7	0.71	0.81
61.70	<i>m</i> -tert-Butylphenol	C <sub>10</sub> H <sub>14</sub> O	585-34-2	PC	19	7	1.74	1.72
62.28	6-tert-Butyltetralin	C <sub>14</sub> H <sub>20</sub>	42044-26-8	ND	15	0	1.03	-
62.31	Phellandral	C <sub>10</sub> H <sub>16</sub> O	21391-98-0	Ter	4	17	0.14	1.98
62.32	3,3,5,7-Tetramethyl-1-indanone	C <sub>13</sub> H <sub>16</sub> O	54789-23-0	Ket	23	17	1.71	1.59
62.47	Piperitone	C <sub>10</sub> H <sub>16</sub> O	89-81-6	Ter	31	37	4.08	5.01
62.55	2-Caranone	C <sub>10</sub> H <sub>16</sub> O	497-62-1	Ter	4	3	0.98	0.38
62.68	<i>p</i> -tert-Butylphenol	C <sub>10</sub> H <sub>14</sub> O	585-34-2	PC	46	67	4.03	12.79
63.00	1,2,3,4-tetramethyl-4-(1-methylethenyl)benzene	C <sub>13</sub> H <sub>18</sub>	61142-76-5	BD	12	17	0.96	1.63
63.23	D-Carvone	C <sub>10</sub> H <sub>14</sub> O	2244-16-8	Ter	62	100	19.90	48.01
63.79	1,1,6-Trimethyl-1,2-dihydronaphthalene	C <sub>13</sub> H <sub>16</sub>	30364-38-6	Nor	65	7	28.58	0.43
64.47	3-Methoxy-5-(trifluoromethyl)aniline	C <sub>8</sub> H <sub>8</sub> F <sub>3</sub> NO	349-55-3	BD	81	93	11.61	17.15
64.62	<i>p</i> -Acetyltoluene	C <sub>9</sub> H <sub>10</sub> O	122-00-9	Ket	8	27	0.84	1.58
64.86	Salicylic acid, methyl ester	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	119-36-8	Est	38	40	5.82	5.63
64.92	2-Methyl-3-phenylpropanal	C <sub>10</sub> H <sub>12</sub> O	100013-18-7	Ald	8	20	0.28	4.26
65.12	1-(2,3,6-Trimethylphenyl)-3-buten-2-one	C <sub>13</sub> H <sub>16</sub> O	54789-45-6	Nor	8	10	1.15	1.63
65.26	1,4-Dimethoxy-2,3-dimethylbenzene	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	39021-83-5	BD	15	3	1.47	0.27
65.83	1-(3-Methylbutyl)-2,3,5-trimethylbenzene	C <sub>14</sub> H <sub>22</sub>	107997-60-4	BD	8	13	1.06	0.88
66.22	$\beta$ -Damascenone	C <sub>13</sub> H <sub>18</sub> O	23726-93-4	Nor	77	63	7.52	10.64
66.48	3,5-Dimethyl benzaldehyde	C <sub>9</sub> H <sub>10</sub> O	5779-95-3	Ald	88	13	8.55	0.68
66.85	1,6,8-trimethyl-1,2,3,4-tetrahydronaphthalene-	C <sub>13</sub> H <sub>18</sub>	30316-36-0	Nor	38	50	2.10	4.13
67.83	2-methoxyphenol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	90-05-1	PC	77	90	5.89	7.91
68.41	1,1-dimethylethyl-4-benzenethiol	C <sub>10</sub> H <sub>14</sub> S	2396-68-1	SC	12	23	0.77	2.47
68.68	1,3,3a,4,5,9b-hexahydro-2H-Benz[e]indol-2-one	C <sub>12</sub> H <sub>13</sub> NO	32940-67-3	Ket	4	0	0.90	-

69.05	1,2,3-Trimethylindene	C <sub>12</sub> H <sub>14</sub>	4773-83-5	Hc	8	40	0.24	2.93
69.36	2,3,6-trimethyl-4-methoxyphenol	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	53651-61-9	PC	31	3	2.43	0.18
69.84	1,1,6,8-Tetramethyl-1,2-dihydronaphthalene	C <sub>14</sub> H <sub>18</sub>	100018-66-3	ND	12	27	0.30	3.01
70.67	Acetate, (2,5,5,8a-tetramethyl-1,2,3,5,6,7,8,8a-octahydro-1-naphthalenyl) ester	C <sub>16</sub> H <sub>26</sub> O <sub>2</sub>	101447-86-3	Est	46	83	2.79	10.14
70.95	Heptanoic acid	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	3665-80-3	CA	19	43	0.87	4.42
71.27	5,6-Dimethyltetralin	C <sub>12</sub> H <sub>16</sub>	20027-77-4	ND	15	23	0.68	2.41
71.38	N-Ethyl-4-nitroaniline	C <sub>8</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	3665-80-3	BD	42	57	2.86	4.60
71.90	2-Methoxy-p-cresol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	93-51-6	PC	4	7	0.12	0.37
72.19	[(tetramethylcyclopropylidene)methyl]benzene	C <sub>14</sub> H <sub>18</sub>	85036-38-0	BD	15	7	1.18	0.30
72.51	2-Bromophenol	C <sub>6</sub> H <sub>5</sub> BrO	95-56-7	PC	77	97	4.41	10.04
72.93	2,4-Dimethyl Quinoline	C <sub>11</sub> H <sub>11</sub> N	1198-37-4	HHc	12	20	1.07	1.96
73.01	1,6-Dimethyl-4-(1-methylethyl)naphthalene	C <sub>15</sub> H <sub>18</sub>	483-78-3	Ses	0	10	-	1.27
73.22	4-Methoxy-2,3,6-trimethylphenol	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	53651-61-9	PC	35	50	1.67	2.41
73.38	2',6'-Dihydroxy-3'-methylacetophenone	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	29183-78-6	BD	31	10	1.61	0.71
73.64	Phenol	C <sub>6</sub> H <sub>6</sub> O	108-95-2	PC	100	97	22.30	20.32
74.11	3,5,8-trimethyl-1,2-dihydronaphthalene	C <sub>13</sub> H <sub>16</sub>	30316-18-8	Nor	0	10	-	0.74
74.26	1,4-Dimethoxy-2,3-dimethylbenzene	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	39021-83-5	HC	8	10	0.63	0.38
74.64	1,7-Dimethylnaphthalene	C <sub>12</sub> H <sub>12</sub>	575-37-1	ND	42	60	4.25	3.43
75.20	Octanoic Acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	124-07-2	CA	23	53	1.56	8.97
75.47	1-Methyl-2-phenylpiperidin-4-one	C <sub>12</sub> H <sub>15</sub> NO	91640-05-0	Ket	81	63	6.85	6.58
75.84	Azunol	C <sub>15</sub> H <sub>18</sub>	489-84-9	Ses	0	27	-	2.00
76.28	2,5,8-Trimethyl-1,4-dihydronaphthalene	C <sub>13</sub> H <sub>16</sub>	30316-19-9	Nor	38	43	4.29	6.41
76.62	p-Cresol	C <sub>7</sub> H <sub>8</sub> O	106-44-5	PC	100	100	71.61	55.20
77.14	1-Ethyl-3,5-dimethylbenzene	C <sub>10</sub> H <sub>14</sub>	934-74-7	Ter	4	0	0.14	-
77.45	Cumic alcohol	C <sub>10</sub> H <sub>14</sub> O	536-60-7	Ter	0	10	-	1.06
77.79	Paeonal	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	552-41-0	Ket	27	10	1.99	0.66
78.06	Eudalene	C <sub>14</sub> H <sub>16</sub>	490-65-3	ND	15	47	1.42	3.25
78.74	3,3,5,6-Tetramethyl-1-indanone	C <sub>13</sub> H <sub>16</sub> O	54789-22-9	Ket	81	87	8.68	8.18
79.48	Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	112-05-0	CA	50	47	4.57	4.24

80.39	2,3,3-Trimethylindanone	C <sub>12</sub> H <sub>14</sub> O	54484-71-8	Ket	8	20	0.14	1.64
80.45	Eugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	97-53-0	PC	0	17	-	1.38
80.47	4,5,5-trimethyl-1,3-cyclopentadien-1-yl-benzene	C <sub>14</sub> H <sub>16</sub>	33930-85-7	BD	38	30	3.14	3.20
80.60	$\alpha,\alpha,\alpha$ -Trifluoro-p-cresol	C <sub>7</sub> H <sub>5</sub> F <sub>3</sub> O	402-45-9	PC	15	10	0.69	0.70

Legend: Alc: Alcohols; Ald: Aldehydes; BD: Benzene Derivatives; CA: Carboxylic Acid; CTRL: control; Est: Esters; FC: Furanic Compounds; Hc: Hydrocarbons; HHc, Heterocyclic Hydrocarbons; Ket: Ketones; ND: Naphthalene Detivatives; Nor: Norisoprenoids; PC: Phenolic Componds; PCa: prostate cancer; SC: Sulfur Compounds; Ses: Sesquiterpenes; Ter: Terpenes; “-”: not identified.