Supporting Information

Table S1: Physical chemical analysis in genipap pulp.

Physical chemical parameters	Mean and standard deviation
Ash (%)	3.26 ± 0.17
Titratable acidity (g Eq. citric acid/100 g)	0.85 ± 0.26
pH	3.95 ± 0.14
Moisture (%)	77.32 ± 0.60
Total soluble solids (ºBRIX)	20.32 ± 0.58
Total phenolics (mg Eq. galic acid/g)	91.71 ± 3.10
ORAC[a] (µmol Eq. Trolox/100 g)	6.71 ± 0.82
Total flavanols (mg Eq. catechin/g)	0.03 ± 0.00
Total flavonols (mg Eq. rutin/kg)	0.54 ± 0.12
Ascorbic acid mg/100 g	0.19 ± 0.06
Carbohydrates (%)	9.16 ± 2.64
Fiber (%)	7.73 ± 1.88
Proteins (%)	2.04 ± 1.09
Lipides (%)	0.67 ± 0.15

[a] Oxygen radical absorbance capacity

Table S2. 50 (P-value < 0.05) most discriminant features in positive mode.

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Genipin isomer	227.0911 (16) 209.0807 (1) 165.0909 (4) 163.0751 (14) 149.0596 (5)	$[M + H]^+$ $[M - H_2O]^+$	4.04	$C_{11}H_{14}O_5$	- 0.9	209.0807 163.0751 149.0596 105.0697	Putatively characterized compound classes (III)
Dihydroxyhydrocinnamic acid	183.0650 (2) 184.0682 (27) 165.0544 (28)	$[M + H]^+$ $[[M + H]+^{13}C]^+$ $[M - H2O]^+$	4.84	$C_9H_{10}O_4$	- 1.0	165.0544 137.0595	HMDB ID: HMDB0000423 (II)
11-Deoxygenipic acid	169.0858 (15) 151.0752 (3) 107.0853 (10)	$[M + H]^+$ $[M - H_2O]^+$ $[M - CO_2]^+$	3.89	$C_9H_{12}O_3$	-1.0	151.0752 107.0853	Putatively characterized compound classes (III)
(1R,6R)-6-Hydroxy-2-succinylcyclohexa-2,4-diene-1-carboxylate	241.0703 (45) 223.0598 (6)	$[M + H]^+$ $[M - H_2O]^+$	4.93	$C_{11}H_{12}O_6$	- 1.3	223.0598 209.0440 195.0643 177.0542 119.0489	KEGG ID: C05817 (III)
3(4)-Dehydrogenipic acid	187.0962 (7)	$[M + H]^+$	3.87	$C_9H_{14}O_4$	- 1.5	169.0856 151.0751 107.0852	Putatively characterized compound classes (III)
14-Deoxygenipinic acid	227.0912 (8) 210.0839 (32) 209.0807 (11) 163.0752 (31) 149.0596 (18) 135.0803 (30)	$[M + H]^+$ $[M - H_2O]^+$	4.68	$C_{11}H_{14}O_5$	- 0.7	209.0807 191.0699 177.0543 163.0750 149.0595 135.0802 121.0646 93.0697	Putatively characterized compound classes (III)
Genipic acid glucuronide	378.1394 (9)	$[M + H]^+$	4.79	$C_{15}H_{20}O_{10}$	0.8	185.0807 167.0698 139.0751 95.0853	(IV)

Table S2. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknown	228.1229 (12)		4.84			183.0649	(IV)
Dihydroxyhydrocinnamic acid isomer	183.0650 (29) 165.0544 (13) 137.0596 (25)	$[M + H]^+$ $[M - H_2O]^+$ $[M - HCOOH]^+$	4.06	$C_9H_{10}O_4$	- 0.8	165.0544 137.0596	HMDB ID: HMDB0000423 (II)
CMPF (3-carboxy-4-methyl-5-propyl-2-furanpropanoic acid)	241.1068 (21) 223.0962 (17)	$[M + H]^+$	4.62	$C_{12}H_{16}O_5$	- 0.7	223.0974 196.1692 181.0861	HMDB ID: HMDB0061112 (II)
11-Deoxygenipic acid isomer	169.0494 (19)	$[M + H]^+$	4.15	$C_8H_8O_4$	- 0.3	151.0751 107.0852	Putatively characterized compound classes (III)
Unknown	225.0755 (20)		4.58			207.0646 189.0543 161.0594 151.0388 119.0490	(IV)
Dimethylphenol	123.0803 (22)	$[M + H]^+$	3.91	$C_8H_{10}O$	-0.9	105.0696 95.0853 81.0696 67.0540	METLIN ID: 88228 (III)
Hydroxyhydrocinnamic acid	167.0700 (23)	$[M + H]^+$	1.79	$C_9H_{10}O_3$	-1.3	149.0132 121.0644 107.0489	HMDB ID: HMDB00375 (III)
Hydroxyphenyl-propanediol	169.0858 (24)	$[M + H]^+$	4.77	$C_9H_{12}O_3$	-0.7	151.0751 123.0802 107.0852	METLIN ID: 984984 (II)
Unknown	169.0494 (26)		3.49			151.0751 124.0867 107.0853 100.0754 94.0285	(IV)

Table S2. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknown	167.0702 (33)		2.22			149.0134 121.0646	(IV)
Prephenic acid	227.0549 (40) 209.0443 (34)	$[M + H]^+$ $[M - H_2O]^+$	1.82	$C_{10}H_{10}O_6$	-0.8	209.0442 191.0334 163.0386 137.0596 135.0438	HMDB ID: HMDB0012283 (III)
Unknown	197.0806 (35)		5.32			190.9925 141.0002	(IV)
Scopoletin	193.0494 (36)	$[M + H]^+$	5.87	$C_{10}H_8O_4$	- 0.6	175.1471 147.0437	HMDB ID: HMDB0034344 (II)
Genipic acid	185.0808 (37) 186.0840 (44) 139.0753 (41) 95.0853 (47)	$[M + H]^+$ $[[M + H]+^{13}C]^+$ $[M - HCOOH]^+$	5.38	$C_9H_{12}O_4$	-0.0	167.0700 139.0753 95.0853	METLIN ID: 91245 HMDB ID: HMDB0036072 (III)
Isoscopoletin	193.0494 (38)	$[M + H]^+$	5.28	$C_{10}H_8O_4$	- 0.6	175.0387 147.0439	KEGG ID: C18079 (III)
Unknown	137.0597 (39)		4.82				(IV)
Unknown	209.0807 (42)		5.32			177.0544 149.0595 141.0002 131.0490 105.0696	(IV)
Unknown	199.0964 (43)		5.58			169.9770 135.0802	(IV)
Unknown	155.0701 (46)		2.60			137.0594 153.0907 135.0805 125.0595 107.0853 89.0707	(IV)
Unknown	171.1013 (48)		4.31			153.0907 125.0595	(IV)

Table S2. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknown	373.1489 (49)		5.72			197.1164 179.1062	(IV)
Unknown	292.1571 (50)		5.73			233.0837 103.0573	(IV)

Levels of metabolite identifications: I, Identified compounds; II, Putatively annotated compounds; III, Putatively characterized compound classes; IV, Unknown compounds.

Table S3. 50 (P-value < 0.05) most discriminant features in negative mode.

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
12-Demethylated-8-hydroxygenipinic acid	243.0510 (7) 244.0545 (13) 199.0613 (9) 155.0714 (1)	$[M - H]^-$ $[[M-H]+^{13}C]^-$ $[M - CO_2]^-$	1.82	$C_{10}H_{12}O_7$	0.0	199.0613 155.0714 137.0607	Putatively characterized compound classes (III)
Unknown	229.0718 (2)		3.13			211.0611 185.0818 150.0559	(IV)
3(7)-Dehydrogenipinic acid	243.0874 (3) 225.0770 (25)	$[M-H]^-$ $[M - H_2O]^-$	4.05	$C_{11}H_{16}O_6$	-0.2	225.0767 149.0606 137.0607	Putatively characterized compound classes (III)
3(4)-Dehydrogenipic acid	185.0819 (4)	$[M-H]^-$	3.89	$C_9H_{14}O_4$	0.3	167.0712 155.0713 141.0920 123.0815 93.0708	Putatively characterized compound classes (III)
3(7)-Dehydrogenipinic acid isomer	243.0874 (5)	$[M-H]^-$	4.67	$C_{11}H_{16}O_6$	0.1	225.0767 213.0767 169.0869 149.0606 137.0607	Putatively characterized compound classes (III)
8-Hydroxygenipic acid	199.0614 (6)	$[M-H]^-$	4.05	$C_9H_{12}O_5$	1.4	181.0505 155.0712 153.0553 137.0606 125.0607 111.0815 93.0709	Putatively characterized compound classes (III)
Unknown	213.0770 (8)		3.91			181.0506 137.0607 119.0500 95.0502 73.0294	(IV)

Table S3. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknown	185.0456 (10)		3.50			167.0348 141.0557 125.0969 123.0815 97.06583	(IV)
Unknown	186.0853 (11)		3.88			168.0747 143.0713 124.0848 94.0742	(IV)
Unknown	227.0563 (12)		2.60			210.0881 183.0661 165.0555 121.0657	(IV)
Unknown	213.0771 (14)		4.34			183.0662 137.0607 73.0294	(IV)
Genipic acid	183.0664 (15)	$[M-H]^-$	5.39	$C_9H_{12}O_4$	0.9	168.0060 155.0348 139.0763	HMDB ID: HMDB0036072 (III)
Hydroxymethyl-cyclopenta[c]furan-1,3diol	171.0664 (16)	$[M-H]^-$	2.59	$C_8H_{12}O_4$	0.8	153.0555 142.9464 109.0657 79.0552	Putatively characterized compound classes (III)
Unknown	345.1191 (17)		5.08			327.1081 285.0978 113.0243 75.0086	(IV)
Unknown	197.0820 (18)		6.61			179.0713 153.092	(IV)
Unknown	211.0614 (19)		4.23			193.0496 181.0507 167.0713 151.0399	(IV)

Table S3. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknown	359.0986 (20)		4.79			183.0662 175.0248 155.0350 139.0764 113.0244	(IV)
Unknown	213.0772 (21)		4.94			133.0489 79.9573	(IV)
Unknown	213.0770 (22)		5.31			195.0665 181.0505 169.0869 151.0764 137.0607 125.0971 119.0502 95.0502 73.0294	(IV)
Nonate	187.0977 (23)	$[M-H]^-$	4.31	$C_9H_{16}O_4$	1.1	169.0869 141.0920 125.0972	METLIN ID: 44183 (II)
Unknown	201.0771 (24)		4.42		1.4	183.0663 157.0869 139.0763	(IV)
Unknown	257.1033 (26)		5.51			221.8424 213.1132 195.1024	(IV)
Hydroxymandelic acid	167.0351 (27)	$[M-H]^-$	4.81	$C_8H_8O_4$	0.7	123.0450 121.0293	HMDB ID: HMDB0000822 (III)
Unknown	227.0928 (28)		5.56			209.1151 183.1026	(IV)
Unknown	213.0405 (29)		4.21			137.0608 125.0607 73.0294	(IV)
Genipic acid isomer	183.0663 (30)	$[M-H]^-$	6.39	$C_9H_{12}O_4$	0.5	169.0010 139.0761 112.9855	HMDB ID: HMDB0036072 (III)

Table S3. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknown	217.1083 (31)		4.74			199.0977 137.0243 93.0345 79.9572	(IV)
3-Hydroxy-4-methoxymandelate	197.0456 (32)	$[M-H]^-$	1.70	$C_9H_{10}O_5$	0.4	179.0350 169.0506 125.0242	HMDB ID: HMDB0029170 (III)
Unknown	123.0451 (33)		4.83			108.0215 95.0138 79.0552	(IV)
2-isopropylmalic acid	175.0613 (34)	$[M-H]^-$	4.87	$C_7H_{12}O_5$	0.9	157.0505 115.0399 85.0658	Identified compounds (I)
Unknown	256.9763 (35)		4.86			177.0192 137.0606 73.0295	(IV)
Unknown	457.1027 (36)		6.31			175.0248 145.0618 113.0244 96.9600	(IV)
Unknown	124.0074 (37)		0.55			106.9807 94.9807 79.9573	(IV)
Unknown	217.1083 (38)		4.31			199.0974 137.0970 97.0657	(IV)
Unknown	401.1821 (39)		5.72			383.1702 341.1605 207.1390	(IV)
2,3-dihydroxybenzoate	153.0195 (40)	$[M-H]^-$	4.59	$C_7H_6O_4$	1.0	137.0352 123.0090 109.0293	Identified compound (I)

Table S3. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknown	371.1346 (41)		5.72			353.1236 311.1132 177.0920	(IV)
3,4-Methylene suberic acid	197.0820 (42)	$[M-H]^-$	6.76	$C_{10}H_{14}O_4$	0.8	179.0721 153.0920 135.0815 59.0137	HMDB ID: HMDB59768 (III)
Unknown	215.0021 (43)		5.04			178.0510 153.0920 135.0450	(IV)
cis-4-Decenedioic acid	199.0977 (44)	$[M-H]^-$	6.95	$C_{10}H_{16}O_4$	1.0	197.0974 181.0869 155.1077 137.0971	HMDB ID: HMDB0000603 (III)
Unknown	211.0614 (45)		4.75			146.0250 132.0453 80.9650	(IV)
Unknown	153.0921 (46)		6.74			135.0815 124.0164 109.0294 59.0138	(IV)
Unknown	133.0507 (47)		1.72			115.0397 87.0086 71.0137	(IV)
Unknown	249.0076 (48)		3.52			169.0141 121.0329	(IV)
3,4-Dihydroxyphenylglycol O-sulfate	249.0076 (49)	$[M-H]^-$	4.01	$C_8H_{10}O_7S$	0.6	169.0506 151.0395 139.0035	HMDB ID: HMDB0001474 (III)

Table S3. continued

Annotated metabolite	MS Main ions *m/z* (*p*-value classification)	Ion	RT (min)	Proposed precursor ion formula	Mass precision (ppm)	MS/MS (*m/z*) main fragments (30-40 v)	Reference/ identification level
Unknowm	377.1454 (50)		6.58			377.1456 183.1026 201.1132 113.0244	(IV)

Levels of metabolite identifications: I, Identified compounds; II, Putatively annotated compounds; III, Putatively characterized compound classes; IV, Unknown compounds.

Figure S1: Common and more specific biomarker of genipap consumption at each time-range. The intersection indicates the steadiest biomarkers across each time-range. Multiplex Pred indicates the predictive multiplex biomarker.

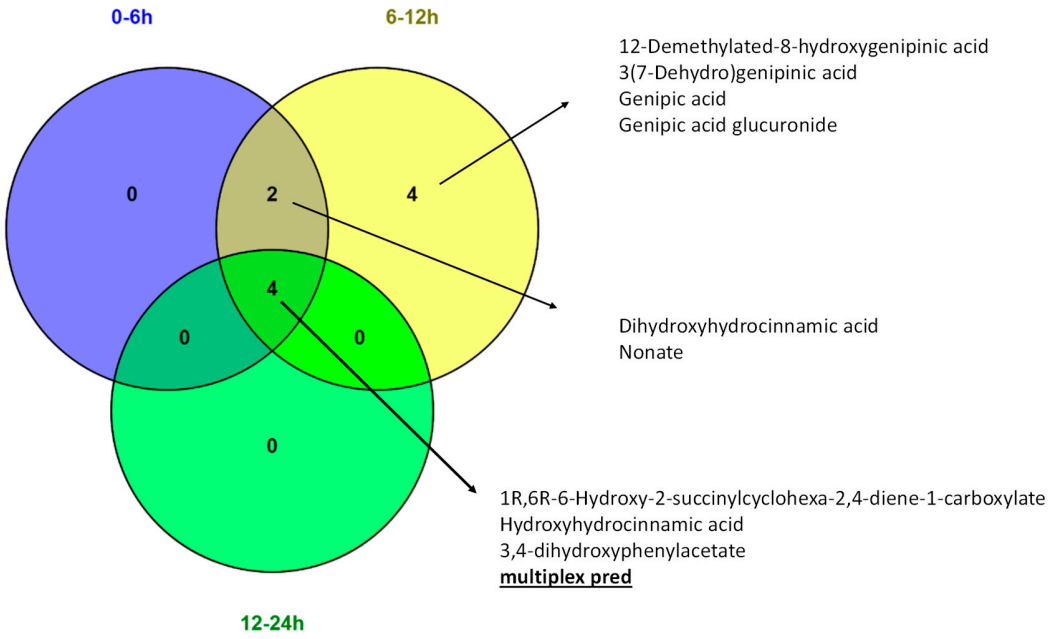


Figure S2: Genipap consumers' vs non-consumers' prediction using the urine multiplex biomarkers measured at 0-6h, 6-12h and 12-24h. The cut off values indicating genipap consumption status were permuted to assess the impact of the sampling time on the prediction over 24h. The actual cut off values of each time-range are indicated in red. Misclassified samples are indicated with an arrow.

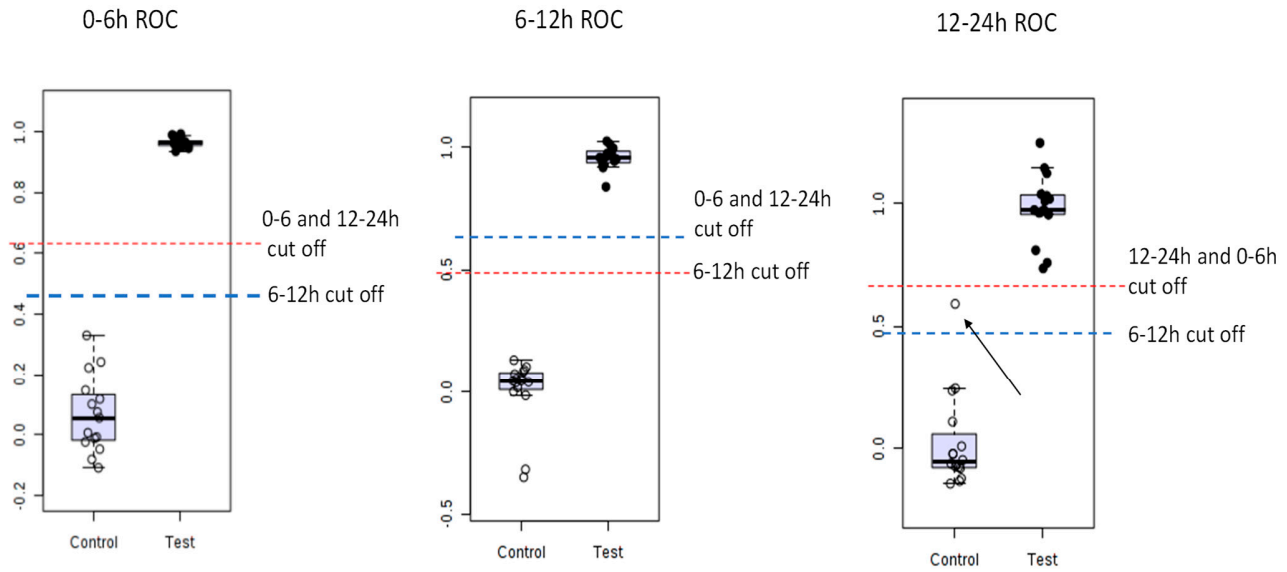
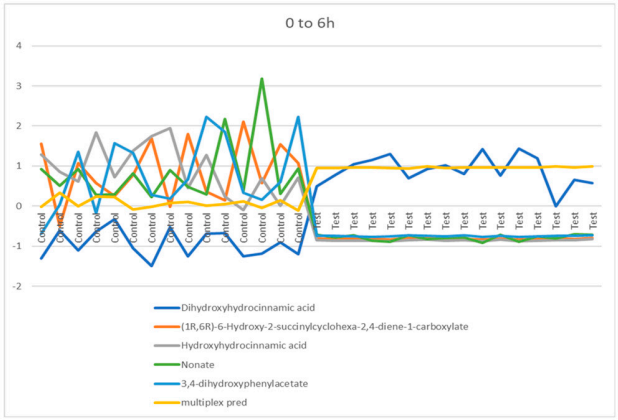
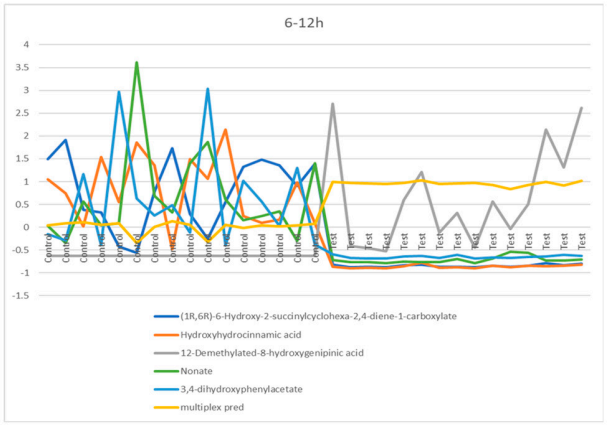


Figure S3: Interindividual variation of best predicting metabolites (ROC AUC of 1, Table 2) at 0-6h (A), 6-12h (B), and 12-24h (C) urine compared to the multiplex biomarker scores (yellow line) calculated over the same time ranges. All values are scaled to 1 to ease comparisons.

A



B



C

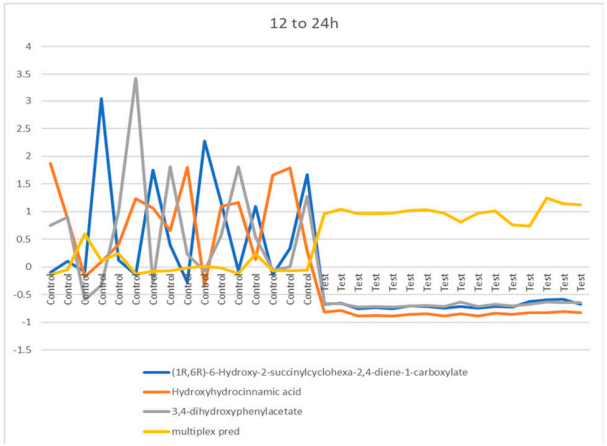


Figure S4: MS/MS spectra fragmentation. (A) spectrum of commercial standard of genipin, (B) spectra of a metabolite obtained from human urine sample after drink genipap juice ([M + H]+, *m/z* 227.0911, retention time: 4.04).