

Supplemental Tables for
Source of ^{12}C in Calvin Benson cycle intermediates and isoprene emitted
from plant leaves fed with $^{13}\text{CO}_2$

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Supplementary Table 1- Parameters used for detection of metabolites with LC/MS/MS.

Parameters for metabolites were optimized using 10 μM standards before analyzing samples.

Metabolite	Cone (V)	Collision (V)	+0 Parent (m/z)	Daughter (m/z)
PGA	26	10	185	97
6PG	34	18	275	97
ADP	42	25	588	346
UDP	42	25	565	323
RuBP	26	18	309	97
Hexose-P	26	18	259	97
Pentose-P	26	18	229	97

Supplementary Table 2 – Isotopologues of metabolites

Relative abundance (per cent of total) for each isotopologue of each metabolite reported in Figure 4 plus the overall degree of labeling in per cent (Total). All data were determined from leaves fed $^{13}\text{CO}_2$ for 20 min. The isoprene data is the same as presented in Figure 5 but included here to allow comparisons. In all but one case there is more fully unlabeled isotopologue than singly labeled. This is also seen in data sets of Ma et al. [1]. They interpreted the fully unlabeled ions as representing inactive pools and called them dilution factors that they removed from of their analyses. Here we interpret these to result from the flux of fully unlabeled carbon skeletons from glucose, through the G6P shunt, to Ru5P entering photosynthetic metabolism. However, at 30°C this effect is smaller than the observed unlabeled isoprene isotopologue, which we attribute to MeCDP metabolism contributing unlabeled carbon skeletons to the isoprene signal. Total label values for isoprene have been corrected for this effect.

A anomalously high value for 6-PG with two ^{13}C labels was observed at both temperatures. If this resulted from some ion other than doubly labeled 6-PG, the data would need correcting. We calculated corrected values for 6-PG by forcing the value for two-labeled 6-PG to be the average of 1- and 3-labeled values (shown as 6-PG-C in the table). The corrected data improved some of the fits we report but because we do not have evidence for a contaminating signal and because all of the statistical tests we rely on in the text hold up (are improved) with the corrected data, we have presented uncorrected data in the paper. PGA = 3-phosphoglyceric acid; ADPG = ADP glucose, presumed to reflect the glucose and fructose 6 phosphate pools of the plastids; UDPG = UDP glucose, presumed to reflect the glucose and fructose 6-phosphate pools of the cytosol; 6-PG = 6-phosphogluconate

Isotopologue	0	1	2	3	4	5	6	Total
<i>30 °C</i>								
PGA	2.1 ± 0.6	1.9 ± 0.5	10.5 ± 2.2	85.6 ± 3.2				93.2
ADPG	2.3 ± 0.2	0.1 ± 0.06	0.2 ± 0.1	1.0 ± 0.6	3.3 ± 0.9	15.9 ± 2.6	77.2 ± 4.3	93.2
Isoprene	6.6 ± 0.8	2.1 ± 1.2	3.1 ± 1.2	11.1 ± 0.8	12.6 ± 2.5	64.6 ± 3.6		89.2
UDPG	23.1 ± 3.8	3.5 ± 0.6	2.46 ± 0.4	3.2 ± 1.7	4.2 ± 0.8	12.5 ± 1.4	51.3 ± 7.5	67.3
6-PG C	33.8 ± 13.4	2.8 ± 1.0	3.5	4.2 ± 1.2	6.2 ± 0.8	9.2 ± 3.6	40.4 ± 12.4	55.9
6-PG	27.4 ± 12.5	2.2 ± 0.9	24.3 ± 6.3	3.3 ± 1.0	4.9 ± 0.8	7.2 ± 2.5	31.6 ± 8.1	50.6
<i>40 °C</i>								
PGA	9.5 ± 1.1	11.3 ± 2.4	27.9 ± 3.4	51.2 ± 5.6				73.6
ADPG	7.4 ± 3.2	2.1 ± 1.2	4.2 ± 1.5	8.9 ± 2.2	16.8 ± 3.9	28.2 ± 3.4	32.4 ± 6.5	73.3
Isoprene	7.0 ± 1.2	7.1 ± 2.2	16.6 ± 2.9	21.3 ± 1.3	21.0 ± 1.9	27.0 ± 5.0		71.8
UDPG	40.5 ± 6.5	6.2 ± 0.4	5.7 ± 1.4	7.5 ± 0.8	9.8 ± 2.2	14.5 ± 2.7	15.9 ± 3.4	41.1
6-PG C	8.9 ± 5.8	0.7 ± 0.3	5.0	10.3 ± 6.4	17.1 ± 6.7	19.1 ± 8.6	38.8 ± 16.3	73.0
6-PG	6.8 ± 4.2	0.6 ± 0.2	27.0 ± 3.1	8.0 ± 5.2	13.3 ± 5.5	14.6 ± 6.4	29.8 ± 12.8	63.9

References cited

1. Ma F., Jazmin L.J., Young J.D., Allen D.K. (2014) Isotopically nonstationary ^{13}C flux analysis of changes in *Arabidopsis thaliana* leaf metabolism due to high light acclimation. *Proc. Nat. Acad. Sci. USA* **111**, 16967-16972 10.1073/pnas.1319485111