Table 3. Results of refinement. The U_{ij} are the coefficients in the expression exp $[-(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$, which multiplies the atomic scattering factor.

U	Temperature parameters U_{ij} (Å^2)				
	Neutrons	X-rays			$\Delta/\sigma(\Delta)$
		Cu	Mo	Combined	
			Nitrogen		
U_{11}	0.049 ± 0.002	0.056 ± 0.002	0.058 ± 0.002	0.055 ± 0.002	+2.1
U_{22}	.055 + .003	.056 ± .002	.051 ± .002	.052 ± .002	−0.9
U_{33}	.115 ± .004	.129 ± .003	.134 ± .003	.133 ± .003	+3.6
U_{13}	−0.003 ± .004	−0.003 ± .002	.001 ± .004	−0.004 ± .002	−0.2
			Carbon		
U_{11}	0.052 ± 0.003	0.054 ± 0.002	0.052 ± 0.002	0.053 ± 0.002	+0.2
U_{22}	.052 ± .004	.076 ± .002	.079 ± .003	.078 ± .003	+5.2
U_{33}	.105 ± .006	.113 ± .003	.108 ± .003	.109 ± .003	+0.6
U_{13}	.002 ± .005	.004 ± .002	−0.003 ± .005	.002 ± .002	0
			Hydrogen		
U_{11}	0.070 ± 0.008	0.075 ± 0.021	0.067 ± 0.018	0.068 ± 0.018	
U_{22}	.075 ± .008	.055 ± .026	.045 ± .024	.032 ± .022	
U_{33}	.199 ± .015	.173 ± .043	.187 ± .042	.167 ± .037	
U_{13}	−0.004 ± .008	−0.002 ± .021	.049 ± .021	.050 ± .018	

"other side" of the atom. These effects are pictured in Fig. 1, which was obtained by subtracting from the electron density, as derived from the x-ray observations, the density calculated with the neutron parameters and spherically symmetric x-ray scattering factors. Relatively large peaks are found in the section through the molecular plane at $z = 0.25$, which is the one reproduced in Fig. 1.

In particular, density is seen to have migrated from the atoms into the bonding region between the carbon and nitrogen atoms, and into the lone-pair region of the nitrogen atom; on the other hand, only a small maximum is observed in the region of the C–H bond. Integration of the electron density, according to a method developed by Coppens and Hamilton (*6*), shows that 0.08 electron is contained in a box, centered at the midpoint of the C–N bond and measuring 0.47 by 1.0 by 1.45 Å, parallel to the bond, perpendicular to the bond in the plane of the molecule, and perpendicular to the plane of the molecule, respectively. One should note that the nitrogen lone-pair peak would be lower or absent, and the C–N bond peaks would be higher, if a prepared-state nitrogen atom, rather than a spherically symmetric atom, had been substracted from the x-ray density.

Quantitative comparison with theoretical difference-density maps is possible; such comparison would, however, be more meaningful if the thermal motion in the crystals were suppressed by collection of the data at lower temperatures. Such collection would (i) provide more-accurate neutron parameters, (ii) reduce anharmonicity effects which are not allowed-for in the thermal-motion treatment of the data, and (iii) reduce the history of thermal motion to be superimposed on theoretical maps before the comparison can be made. Unfortunately *s*-triazine was found to undergo a phase transition on cooling at about −40°C, but low-temperature work on other, similar, molecules is now in progress.

For detailed analyses of charge distributions one should determine the positional and temperature parameters from neutron-diffraction data only. The x-ray least-squares refinement can then be based on the occupancy factors of localized molecular orbitals, orbital exponents, and similar parameters. A need exists for suitable algorithms for such a treatment that will permit direct comparison with the corresponding theoretical values.

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7 August 1967

Gibberellin Delays Ripening of Tomatoes

Abstract. *Treatment with gibberellic acid, at concentrations as low as 10^{-7}M, of intact tomato fruits, or of pieces in tissue culture, markedly retarded ripening in terms of development of redness. Ethylene stimulations of color development were prevented by treatment with gibberellic acid, but ethylene stimulations of respiration were not. Gibberellin can delay the progress of some components of the ripening of fruit, preventing some of the changes triggered by ethylene.*

In many fleshy fruits, ripening is probably regulated by the production of ethylene, which then triggers a dramatic respiratory rise (*1*); yet there is evidence of the existence in fruits, especially in those remaining on the plant, of factors that defer readiness for ripening (*2*). In tomato fruits, ripening can be deferred by application of inhibitors such as dinitrophenol (*3*). Recent reports that application of gibberellin could cause regreening in citrus fruits (*4*) suggested the possibility that gibberellins may defer ripening. This possibility was especially appealing in view of the reports of declines in content of natural gibberellin in fruits during maturation (*5*).

The dipping of mature green fruits of tomato (*Lyspersicon esculentum* L. var. Ailsa Craig) into solution of gib-

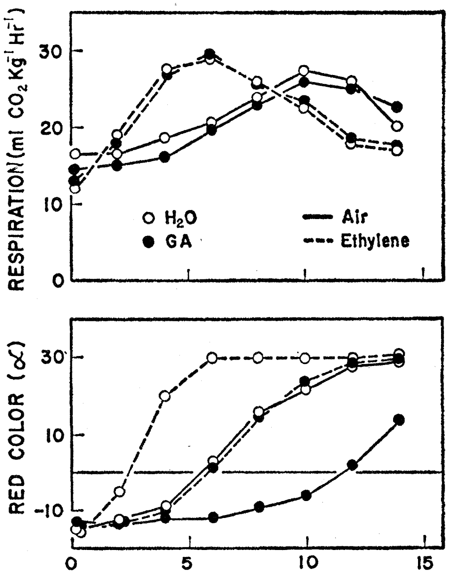

Fig. 1. Ripening of intact tomato fruits, as modified by treatments with gibberellin and ethylene: data for respiration (top) and for development of redness (bottom). *GA*, gibberellic acid.

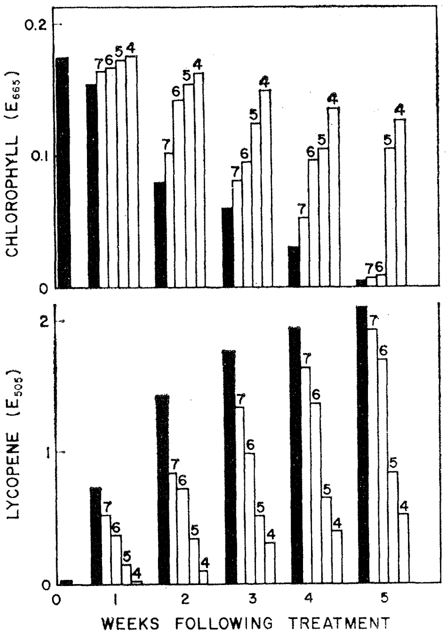

Fig. 2. Changes in pigmentation of slices of tomato fruit in sterile tissue culture, as modified by gibberellin: data for chlorophyll content of hexane-acetone extract (top) and for lycopene content over a 5-week period (bottom). Gibberellin concentrations of 10^{-7} to $10^{-4}M$ indicated as log superscripts; black columns are untreated controls.

berellin ($10^{-4}M$ in carrier) altered the development of red color and respiration (Fig. 1). Shell color was measured with a Hunter Color Difference Meter, using the alpha reading (reflectance at 500 to 675 $m\mu$) as an index of redness; for each datum point, readings were made on 24 fruits. Figure 1 (bottom) shows that the fruits treated with gibberellin developed half-red color in approximately 14 days, in contrast to the water-treated controls which reached half-red color in approximately 8 days. Ethylene-treated fruits [ethylene at 1000 parts per million (ppm) for 24 hours] reached a similar color within less than 3 days, and this enhancement by ethylene was eliminated by treatment with gibberellin.

Respiratory responses to gibberellin and ethylene were markedly different (Fig. 1, top); rates of evolution of carbon dioxide were measured in a flow-through infrared gas analyzer. Evidently the respiratory climacteric proceeded unchanged after treatment with gibberellin, and the enhancement by treatment with ethylene of the onset of the climacteric rise was likewise unchanged by the treatment with gibberellin.

When various means of application of the gibberellin were compared, the greatest responsiveness was found in discs of fruit tissue treated under sterile tissue-culture conditions. Figure 2 (top) shows that the chlorophyll content of the tissue pieces, measured as the light absorbance at 665 $m\mu$ by hexane-acetone (4 : 5) extract (10 g of tissue in 50 ml of solvent) remained high in response to applications of gibberellin at concentrations as low as $10^{-7}M$. The rise in lycopene, measured as absorbance at 505 $m\mu$, also was deferred by the entire range of concentrations of gibberellin tested. After 5 weeks at 20°C, tissue treated with $10^{-5}M$ gibberellin had lost only about 30 percent of its chlorophyll and accumulated 30 percent of its lycopene. The rise in carotenoids, measured as absorbance at 475 $m\mu$, was similarly deferred by treatment with gibberellin.

Ripening of gibberellin-treated fruits could be restored to a normal rate by the subsequent application of ethylene at 1000 ppm for 24 hours.

These results show that part of the ripening process in tomato fruits can be depressed by gibberellin. The singular insensitivity of the respiratory climacteric to gibberellin indicates that the ripening processes are not all closely linked with the respiratory shifts associated with the climacteric (*6*).

Scott and Leopold (*7*) have pointed out that it is common for gibberellin and ethylene to act in opposite manners on various physiological processes; the ability of ethylene to stimulate the pigmentation changes associated with ripening can be opposed by gibberellin. The actions of ethylene on the respiratory climacteric are not opposed by gibberellin. Evidence (*8*) that the climacteric occurs principally in the mitochondria of tomato fruits suggests that there may be differences between cellular compartments with respect to their responsiveness to additions of ethylene and gibberellin (*9*).

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21 September 1967

Sulfide Solubilities in Alteration-Controlled Systems

Abstract. *Solubilities of sphalerite (ZnS) and galena (PbS) were determined at 300° to 500°C and 1000 bars total pressure in a chemical environment buffered by silicate mineral equilibria. Chloride solutions and muscovite-bearing assemblages characteristic of hydrothermal wall-rock alteration were used; weak acidities at temperature were therefore involved. The metal concentrations encountered tended to be higher than those observed in high bisulfide–H_2S systems at neutral to weakly basic* pH *used in most previous experimentation; the chemical conditions of the work, although not completely satisfactory, are geologically more realistic than previous experimentation done in the basic-*pH *region.*

The nature of ore-forming solutions has long been a topic of interest and controversy among geologists. Considerable attention has been recently directed toward experimental evaluation of sulfide solubilities at elevated temperatures and pressures (*1–3*). The chemical environment used in most of these investigations has been neutral to high in *p*H and relatively high in total sulfide. These conditions have been primarily based on chemical arguments that sulfide complexing of certain metal is known to occur in sulfide-rich solutions of high *p*H.

A somewhat different view from this one is the hypothesis that most hydrothermal ore-forming solutions are predominately chloride solutions, weakly to moderately acid at the site of ore deposition. Garrels (*4*) long ago reasoned that the highly saline fluid in-