

evidence that this group is retained in the lattice interstitially, so that its position depends on the molecular packing and is, therefore, different in different forms.)

This correspondence would appear to prove: (a) that the two-dimensional Fourier projection of Fig. 1 is nearly correct; (b) that the myoglobin molecules in two different species, seal and sperm-whale, are closely similar in general configuration even though their amino-acid compositions are known to differ in details; (c) that the outline of the molecule deduced by Kendrew is very nearly right, because there could not be so close a fit if it had been incorrectly traced and included portions of neighbouring molecules.

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EFFECTS OF GAMMA-RADIATION ON SOME CARBOHYDRATES, HYDROXYACIDS AND AMINO-ACIDS IN AQUEOUS SOLUTIONS

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IN an investigation of the effect of γ -radiation from a 200-c. cobalt-60 source on dilute (0.1 per cent) aqueous solutions of some carbohydrates, hydroxyacids and amino-acids we have found that in the absence of oxygen (that is, *in vacuo* or under nitro-

gen), radicals¹ derived from these compounds exhibit a strong tendency to dimerize (irradiation dose 5.5×10^{19} eV. ml.⁻¹) and that prolonged irradiation produces polymeric materials. Acidic non-dialysable polymers have been isolated (see Table 1), which

Table 1. IRRADIATION OF CARBOHYDRATES, HYDROXY- AND AMINO-ACIDS IN AQUEOUS SOLUTION

Solute irradiated	Conditions	Polymer formation indicated by dialysis cetavlon		Other compounds formed, remarks, etc.	Periodic acid treatment (see text)
Maltose	Vacuum	Yes	Yes	Glucose, gluconic acid, maltobionic acid, <i>et al.</i>	
Glucose	Vacuum	Yes	Yes	Gluconic acid, 2-oxo-D-arabino-aldohexose, 2-oxo-D-arabino-hexonic acid, arabinose, <i>et al.</i>	
Glycollic acid	Oxygen	No	No	Gluconic acid, <i>et al.</i>	
	Nitrogen	Yes	Yes	As vacuum system	Yes
Glyoxylic acid	Vacuum	Yes	Yes	Glyoxylic, tartaric, oxalic and formic acids, formaldehyde and CO ₂	
	Oxygen	No	No	As for vacuum system, but only traces of tartaric acid	
Tartaric acid	Vacuum	—	—	Oxalic acid, reducing acidic dimer and trimer. Dimer may be dihydroxytartaric acid	Yes
	Oxygen	—	—	Oxalic acid, no other non-volatile products detected	
Oxalic acid	Vacuum	—	—	Non-acidic reducing compound with $R_r = 1.6$, reducing material with $R_r = 1$. Main product had $R_r = 0.3$, $MR = 1.0$ ('dimer'?)	Yes
	Oxygen	—	—	Mesoxalic acid, glyoxylic acid, considerable reducing material with $R_r = 1$	
Lactic acid	Vacuum	—	—	Small amounts of a reducing compound formed, having $R_r = 0.6$	
Gluconic acid	Vacuum	Yes	Yes	Considerable loss of oxalic acid, but no other non-volatile compounds detected	
Mandelic acid	Vacuum	?	?	Not examined	
Formic acid	Vacuum	—	—	Arabinose, arabonic acid, <i>et al.</i>	
	Oxygen	—	—	Heavy precipitation from aqueous solution, CO ₂ formed. Precipitate contains C ₆ H ₈ and COOH groups	Yes*
Glycerol	Vacuum	—	—	Mesoxalic acid, dihydroxytartaric acid and probably tartaric acid. Striking between $R_r = 0$ and 1.5	
	Oxygen	—	—	No non-volatile products	
Glycollic acid and glyoxylic acid†	Vacuum	—	—	Glyceraldehyde, glyceric acid, at least two non-reducing compounds behaving as hexitols. Traces non-reducing acids	
	Vacuum	—	—	Dihydroxytartaric acid. Slight uptake of bromine water, suggesting some dihydroxymaleic acid	
Glyoxylic† and tartaric acids	Vacuum	—	—	Glyoxylic acid, slightly reducing acidic component with $R_r = 0.7$, suggesting a 6-C co-dimer. Reducing compounds with $R_r = 1$.	
	Vacuum	—	—	As for glycollic and tartaric acids system, but more reducing compounds at $R_r = 1$ and 0.7	
Glycerol and 1:3-dihydroxyacetone†	Vacuum	—	—	Hexonic acids, small amounts of glyceric acid. Hexose production uncertain	
	Vacuum	—	Yes	As for glycerol and glyceraldehyde system. Ketohexose production doubtful	
Alanine	Vacuum	—	No	Compounds or compound with $R_{glycine} = 0.5$ detected with ninhydrin and alkaline silver nitrate	
	Oxygen	—	Yes	No compounds with $R_{glycine} < 1$	
Phenylalanine	Vacuum	—	Yes	Not examined	
	Vacuum	—	Yes	Not examined. No precipitation, but the freeze-dried solute was only sparingly (0.2 per cent) soluble in water (cf. mandelic acid)	

* Forms glyoxylic and oxalic acids.

† Indicates the component in mixed systems which was the more readily destroyed by radiation.

gave precipitates with 2 per cent 'Cetavlon' solution², the precipitates being soluble in *M* sodium chloride. The presence of oxygen drastically reduced dimerization, and no polymers were then detected. Instead, oxidation products were formed by processes which involved considerable C—C bond scission and decarboxylation. These effects can be readily explained by the radicals initially produced from the solvent causing hydrogen abstraction from the organic solute, thereby forming an organic radical³. *In vacuo* or under an atmosphere of nitrogen these radicals may join together or undergo saturation by the addition of a solvent radical. In the presence of oxygen, the gas readily adds on to the organic radical to yield a peroxy-radical, which may react with radicals⁴ present in the system to yield a molecule in which, ultimately, a hydroxy group has been substituted on to the site of the original hydrogen abstraction.

The emphasis in this work has been on the radical addition reactions occurring *in vacuo*, including reactions occurring in solutions containing more than one solute when dimers are formed by linking of the various radicals. The glucose and glycollic acid systems have been examined, and in the latter case a complete mass balance in the presence and absence of oxygen has been obtained¹. Polymeric materials have been isolated as indicated, but the evidence for compound formation is based on chromatographic and ionophoretic analysis. The mobility values quoted, R_T and M_T , are the chromatographic (propionic acid/*n*-butanol/water—3 : 6 : 4 v/v) and ionophoretic (0.2 *M* acetate buffer, pH 5.0) mobility values respectively, relative to tartaric acid. The spray reagents used were aniline hydrogen phthalate⁵

(reducing sugars), alkaline silver nitrate⁶, and chlorophenol red⁷ (acidic groups). In addition, in some cases the solute mixture, after being spotted on to the paper, was treated with a spot of 5 per cent periodic acid pentahydrate solution before irrigation and subsequent spraying⁸. This method causes tartaric acid to yield glyoxylic acid and dihydroxytartaric acid to yield oxalic acid, etc. In the amino-acid systems, the chromatograms were sprayed with ninhydrin⁹ and alkaline silver nitrate⁶, and the mobilities expressed as R_{glycine} relative to glycine using the propionic acid/*n*-butanol/water solvent.

The results are shown briefly in Table 1, and indicate the potentials of mixed solute irradiations in vacuum for forming radical addition products, and the readiness with which polymers can be formed. It is hoped that further work will elucidate more thoroughly the structure of the polymers and the addition compounds formed.

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SOME SOUTH AFRICAN STONE AGE CULTURES

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Statistical Analysis of the South African Later Chelles-Acheul and Earlier Fauresmith Cultures

IN South Africa our knowledge of the Earlier Stone Age is based on pioneer work that yielded the framework of stratigraphy and broad typo-technological outline of the main prehistoric cultures. Pioneer research regarded the Fauresmith Culture as well separated typologically, technologically and stratigraphically from its ancestor, the Chelles-Acheul. In the Vaal River Basin the South African Chelles-Acheul Stages III-V industries, here described as Later Chelles-Acheul, are found in the later aggradations of the Younger Gravels and overlying calcified sands with a predominantly Middle Pleistocene fauna¹, while the Earlier Fauresmith lies on the surface of the calcified sands and in the Youngest Gravels of the Vaal tributaries².

Recent excavations at two Transvaal sites, the Cave of Hearths near Potgietersrus and Wonderboom near Pretoria, have yielded important Earlier Stone Age industries originally classified as Later Chelles-Acheul on a non-statistical basis^{3,4}. Subsequent study of the Cave of Hearths Earlier Stone Age fauna showed it to be of Later Pleistocene age

(Cooke, H. B. S., personal communication), that is, considerably more recent than the Vaal Chelles-Acheul fauna. Industries similar to the Cave of Hearths Earlier Stone Age were found in Later Pleistocene gravels at open sites near the cave. This dating evidence, apparently conflicting with the typology of the industries, led to a detailed statistical study of both the Cave of Hearths and Wonderboom industries, which were statistically compared with Later Chelles-Acheul industries from Vaal Middle Pleistocene gravels at Riverview Estates and Canteen Koppie. It was then found that, despite very close overall resemblances in typology and technology, the Vaal Later Chelles-Acheul and Wonderboom-Cave of Hearths series could be statistically separated, in terms of hand-axe length-width proportions and proportions of dorsally prepared quadrilateral flakes. A Later Pleistocene gravel series from Rooiberg, geographically situated between Wonderboom and Cave of Hearths, was found to have the same statistical characters as those from the latter two sites. Clearly these three industries, all originally classified in non-statistical terms as Later Chelles-Acheul, must be re-classified as Earlier Fauresmith, a culture probably less than half the age of the Later Chelles-Acheul.