FERROMAGNETIC RESONANCE IN DNA SAMPLES

by

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Several investigators (Bliumenfeld, 1959; Müller, Hotz and Zimmer, 1961; Blois and Maling, 1961) have recently reported observing broad electron spin resonance signals in unirradiated desoxyribonucleic acid (DNA) and related compounds. From the measured microwave absorption intensities, the densities of unpaired electron spins have been calculated to be as high as 10^{20} per gram, based on the assumption that the magnetic centers are paramagnetic. Although the origin of these signals had not been definitely determined, it was nevertheless inferred from the high concentrations that the magnetic centers were intrinsic to pure DNA.

We would like to report similar spin resonance measurements on DNA. However, our signals arise from a ferromagnetic constituent. While they are as intense as those observed previously, spin densities calculated on this basis are almost one thousand times lower than those calculated assuming paramagnetic spins. These smaller spin concentrations do not exceed the concentrations of iron atoms present as impurities in the DNA samples.

In Fig. 1 are displayed electron spin resonance spectra measured in vacuo at 11.7 kMc in a 250 milligram sample of low molecular weight DNA extracted from herring sperm (Nutritional Biochemical Co., Cleveland). At room temperature

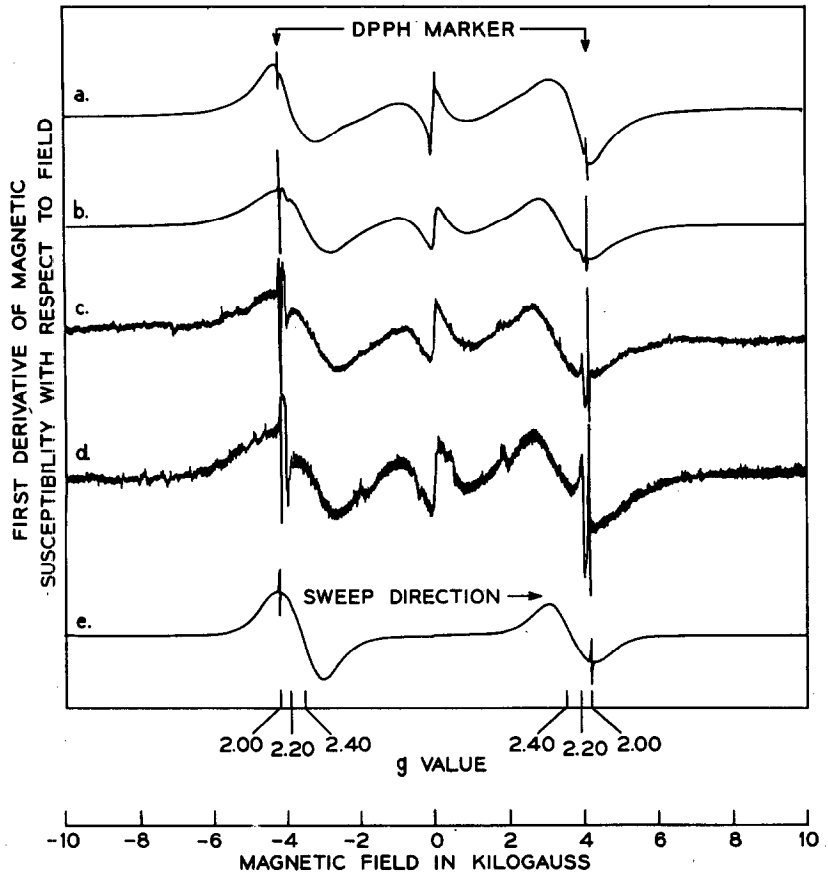

Fig. 1

Curves(a) through (d) are traced recordings of the resonances at 300,77,20 and 4.2°K,respectively,of DNA extracted from herring sperm.The structure seen near zero applied field may be removed by versene. It can also be removed by filtering a water solution of the DNA so as to remove water insoluble solids. The paramagnetic line at g=2.07. is also removed by versene. At 20°K and 4.2°K the paramagnetic line was easily saturated. To avoid saturating this resonance the microwave power was lowered thereby decreasing the signal to noise in(c) and (d). The intensity of the broad resonance centered near g=2.2 to 2.5 is independent of temperature. Its characteristics resemble those of an iron hydroxide suspension shown in curve (e). In this trace,taken at 77°K,one can see the hysteresis of line intensity which has also been found in other DNA samples.

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the broad resonance has a g-factor of 2.20±0.05 and a line width between points of maximum slope of roughly 1200 gauss. As the temperature was lowered to 4.2°K, both the g-factor

and the line width increased. The integrated intensity of the broad line, however, remained constant within ±20% as the temperature was lowered. The intensity was measured relative to that of DPPH free radical whose intensity exhibits the 1/T dependence characteristic of a paramagnet. As can be seen in Fig. 1, the resonance is very broad and extends down to zero magnetic field. A hysteresis in line intensity has been observed in other DNA samples. Similar broad resonances are found in ferromagnetic substances (as an example Fig. 1(e) shows the spectrum of a iron hydroxide suspension in soap solution). The g-factor is compatible with an iron group ferromagnetic compound or metal since values of g between 2.1 and 2.2 are characteristic of these materials (Kittel, 1953).

Further evidence for the ferromagnetic nature of our sample of herring sperm DNA is found in the measurements of the static susceptibility. At room temperature a magnetization of $\sim 1.5 \times 10^{18}$ Bohr magnetons per gram was measured and found to be independent of magnetic field between 3000 and 14,000 gauss. A similar field-independent moment was observed previously (Bliumenfeld, 1959). A more dramatic display of the ferromagnetic behavior at 300°K was obtained by first placing a plastic capsule containing the DNA sample in a strong magnetic field. The sample was removed from the field and suspended from a string so that it was free to rotate like a compass needle. The north pole of a bar magnet attracted one end of the sample while the south pole attracted the other. The coercive force of the DNA sample was 170 gauss. In this herring sperm sample, both the static susceptibility measurements and the resonance intensities indicated about 10^{18}

spins per gram.

In addition to the broad ferromagnetic resonance signal, another narrower resonance with a temperature independent g-factor of 2.070±0.005 and a line width of 90 gauss was observed at 77, 20 and 4.2°K in the herring sperm sample. The intensity of this line was proportional to 1/T as expected for a paramagnetic material. It can be seen, however, that its integrated intensity is considerably less than the broad line. Additional evidence for a paramagnetic constituent of the sample was obtained from the magnetic susceptibility measurements which showed a temperature dependent contribution below 20°K.

The DNA sample was dissolved in water and treated with versene in order to remove the iron. Chemical analysis showed that no appreciable fraction of the iron was removed. The ferromagnetic resonance changed only in that the zero field structure was eliminated, but the weaker, paramagnetic resonance disappeared. In a subsequent sample dissolved in water, we found small pieces of ferromagnetic solids which were removed by filtration. This removed the zero-field structure but did not affect any other features of the spectrum.

Similar broad temperature independent electron resonances were observed in three other samples of DNA - two fibrous samples of calf thymus DNA (Sigma Chemical Company, St. Louis) and one DNA sample extracted from salmon sperm (California Corporation for Biochemical Research, Los Angeles).

The herring sperm sample was the lowest quality of those studied thus far and exhibited the greatest variety of structure. The broad ferromagnetic resonance was the common feature seen in all samples.

In these four samples, X-ray fluorescence analysis

indicated that the major impurity was iron, while chemical analysis revealed that the iron was present in concentrations in the range of 10^{16} to 5×10^{18} atoms per gram. In general, the iron concentration was high enough to explain the observed ferromagnetic resonances and a detailed quantitative correlation amongst these three measurements is being sought. At present we are unable to be more specific about the origin of the ferromagnetic resonance signal.

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