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Isolation of an Iron Pigment From Human Red Hair.

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Since 1878 it has been known that a red substance can be extracted with mineral acids from human red hair.[1,2] This pigment is not obtainable from red hair of animals or from any human hair except bright red.

Experiments. In the authors' experiments red hair was treated with chloroform, acetone and glacial acetic acid respectively in the cold for fat removal, dehydration and initiating keratolysis. The colored matter was then completely extracted within 2 hours by boiling the hair with 0.1 N HCl in a reflux condensor. The color of the hair was not modified by this procedure.

The purplish-red clear extract (pH 1.5) turned brown on addition of alkali at pH 2.6 and regained its original red color on re-acidification. Further alkalinization precipitated the pigment at pH 7.0. Above this pH it again went into solution with a brown color. The sharp isoelectric point made the purification of the substance possible by repeated washing, dissolving, and re-precipitating.

The purified dry material, an amorphous dark red-brown powder with a metallic sheen, was insoluble in water, in organic solvents, and in acetic acid; it was easily dissolved by alkalies and by triethanolamine, a brown color resulting. Solution of the dry substance in acids was difficult but was easily accomplished after previous solution in alkali. The dry pigment kept indefinitely at room temperature. Heated, it decomposed without melting and left a reddish-brown ash. One hundred grams of hair yielded about 40 mg of pigment.

Qualitative analysis revealed iron in a complex form. The thiocyanate test for ferric ions was positive whether the hair had been extracted in the presence or absence of oxygen.

Red acid solutions showed a narrow absorption band with a maximum at 535 mμ. This band disappeared from the spectrum after alkalinization.

The pigment was dialyzable. In a cataphoresis experiment the color migrated to the anode at pH 9.16.

On addition of strong mineral acids or of an excess of thiocyanate, a brown substance precipitated, which was soluble in alkalies only. From the supernatant fluid of either precipitate another red substance could be precipitated at pH 7, showing the same properties as the original pigment except for a stronger thiocyanate reaction.

The diazo reaction and reactions for aldehyde, ketone groups, for tyrosine, catechol, pyrrol and indole nuclei were negative. The solutions did not show fluorescence in ultraviolet light.

Quantitative microanalysis of the purified pigment was performed on 2 samples from different groups of individuals.*

Purified Pigment.

	C	H	N	Ash
First sample	45.06	5.04	7.43	7.31%
Second sample	45.27	4.88	7.06	13.11 (Fe 9.17)%

In a 5-minute micro-Van Slyke experiment the pigment yielded 0.32% amino nitrogen.

Quantitative analysis of the red cleavage products gave these results:

Cleavage Products.

	C	H	N	Ash
Decomposition by HCl	32.05	3.91	7.74	26.46 (Fe 18.51)%
Decomposition by KSCN	33.97	3.93	5.65	31.41 (Fe 21.30)%

Despite the great difference in iron content

[1] Sorby, H. C., *J. Anthropol. Inst. of Great Britain*, 1878, **8**, 1.

[2] Arnow, L. E., *Biochem. J.*, 1938, **32**, 1281.

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the C:H:N ratio in the original material and in the KSCN cleavage product was almost identical: 7.5:10:1 versus 7.1:10:1. The brown precipitate formed during the HCl cleavage yielded C: 47.27, H: 5.32, ash: 2.90%.

The difficulty in calculating empirical formulas indicates we must further purify the material. For the original pigment the tentative formula is suggested: $(C_{15}H_{20}N_2O_9)_2Fe$.

Comment. The purplish-red color of the iron-pigment, the reversible color change with the pH and the type of the absorption spectrum[3] strongly suggest that it belongs in the group of complex phenolic iron compounds. In such compounds a single ferric ion is complexly bound to a varying number of phenolic radicals.[4] The data of the cleavage products indicate that during decomposition some phenolic groups separate from the iron, whereas others do not. Thus in the supernatant fluid new compounds of smaller molecular weight are present with all the properties of the original pigment (including similar absorption spectra) but containing more iron.

Phenolic iron compounds, however, are less stable than the pigment of red hair. The latter's greater stability may be explained by assuming that the phenolic OH-group is attached to a heterocyclic ring containing nitrogen. The negative reactions for pyrrol and pyridine do not exclude such a possibility because substitutions on these rings modify their reactivity. At present, no definite statement can be made regarding the chemical structure of the iron-containing pigment of red hair.

Summary. A red iron pigment was isolated from human red hair. The presented data indicate that it may be a complex phenolic iron compound in which the phenolic OH group is attached to a heterocyclic ring containing nitrogen.

3 Wesp, E. W., and Brode, W. R., *J. Am. Chem. Soc.*, 1934, **56**, 1037.

4 Weinland, R. I., and Herz, A., *Liebig's Annalen*, 1913, **400**, 219.

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Physiological Studies on Five Patients Following Ligation of the Inferior Vena Cava.

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The effects of ligation of the inferior vena cava of the experimental animal upon the circulation and functions of the parts drained by its tributaries have been studied by many.[1,2] If the ligation is below the renal veins, there are no apparent serious results. The inferior vena cava has been ligated relatively frequently in man.[3,4] It has been noted that when the ligation is below the renal veins, there is little disturbance experienced by the patients. It is the purpose of this report to record briefly a few physiologic observations made on 5 patients in whom the inferior vena cava was ligated by Dr. C. G. Collins of the Department of Gynecology and Obstetrics of Tulane Medical School.

Methods. The patients were studied several days after operation when they were sufficiently well to be moved from Charity Hospital to a laboratory specially equipped for such observations. These people were too ill to be moved from the hospital to the laboratory for study before operation.

1 Polkey, H. J., *Urol. and Cutan. Rev.*, 1929, **33**, 394.

2 Whittenbergr, J. L., and Huggins, C., *Arch. Surg.*, 1940, **41**, 1334.

3 Krotski, J., *Chirurg.*, 1937, **9**, 425.

4 Ochsner, A., and DeBakey, M., *New England J. Med.*, 1941, **225**, 207.