The Dreywood Anthrone Reaction as Affected by Carbohydrate Structure

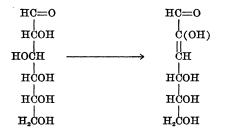
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The recent work of Roman Dreywood (1) and of Daniel Luzon Morris (3) has shown that anthrone in sulfuric acid is a general reagent for carbohydrates, including sugars, polysaccharides, glycosides, carbohydrate ethers, and esters. The writers have confirmed this by tests with methylated glucose, diheterolevulosan, levulose tetraacetate, maltose octaacetate, hydroxymethylfurfural, and the diphenylacethydrazide of hydroxymethylfurfural. However, the phenylosazones of glucose and galactose and the phenylosotriazole of glucose do not give this test, whereas mannose phenylhydrazone gives a positive reaction. These facts must be connected in some way with the structure of these compounds. The osazones and osotriazoles differ from the other compounds by yielding osones with strong acids, while the hydrazones are reconverted to the original sugars. These, in common with the other carbohydrates and carbohydrate derivatives mentioned previously, initially split off water, with the formation of hydroxyaldehydes, with glucose for example:



This was postulated by Hurd and Isenhour (\mathcal{Z}) and confirmed by Wolfrom, Schuetz, and Cavalieri (5). By further loss of water and ring formation the hydroxyaldehyde goes over to hydroxymethylfurfural. In an analogous manner pentoses yield furfural, and hexomethyloses yield methylfurfural. The anthrone reaction thus substantiates this mechanism.

Incidentally, the anthrone reagent gives a cherry-red color with ascorbic acid and a negative test with levulinic acid, acetol, and methylglyoxal.

The study of the anthrone reaction further suggested the testing of melanoidins for residual sugar groups, since these substances are high polymers and Dreywood (1) obtained a positive reaction with cellulose plastics. The natural melanoidin extracted by Weast and MacKinney (4) from sun-dried apricots gave a negative test,

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but the synthetic melanoidin prepared by heating a solution containing fructose and aspartic acid, and having practically the same elementary composition as the natural product, gave a positive carbohydrate reaction.

In view of the fact that the anthrone reaction seems to require the presence of a furfural structure, the above observations lend support to our belief that melanoidins may be produced in two ways. The first way is through the formation of 3-carbon fragments (acetol, glucic acid, methylglyoxal) which polymerize and then react with amino acid. The reaction is favored by mild temperature conditions such as obtain in the drying of apricots. The second route leading to melanoidin formation requires higher temperatures, and under these conditions hydroxymethylfurfural is formed, which then yields melanoidins by reacting with amino acid.

References

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Inhibition of Hair Growth by the Percutaneous Application of Certain Adrenal Cortical Preparations

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Accumulating evidence suggests that the adrenal cortex may act as an inhibitor of hair growth. Butcher (2) and Ralli and Graef (5) found in the adult rat that replacement of hair on depilated areas of skin is accelerated by adrenalectomy. Another report by Butcher (4) points to the cortical part of the gland as being responsible for this effect. He also found (3) that the skin of the adrenalectomized rat exhibits an increased rate of oxygen consumption paralleling the increased rate of hair growth. Ralli and Graef (5) observed that melanin deposition in hair is also stimulated by adrenalectomy under conditions that ordinarily inhibit its production. The same workers (6) discovered that injected desoxycorticosterone acetate and, to a lesser degree, adrenal cortical extract prevented the stimulation of hair growth and melanin deposition which otherwise follows adrenalectomy in the black-hooded rat. The following experiment was conducted to determine whether or not various adrenal cortical preparations might exert an inhibiting influence on hair growth when applied directly to the skin.