

in the two curves and of the structural relations that can be deduced from them will be deferred until a later date when the several alkali silicate systems can be covered. It is sufficient for the purposes of this discussion to point out that the break at .433 is most probably related to saturation of the cristobalite-like structure of silicate glass with sodium atoms. Above this ratio, the introduction of sodium does not cause much expansion of the framework, since there is sufficient void space to accommodate the additional atoms. Most of the lowering of framework density can be accounted for by the removal of silicon atoms. Below the critical ratio, however, it is necessary for the whole structure to expand as additional sodiums are added, because the voids in the framework are full. Changes in the numbers of oxygen atoms shared by each tetrahedron apparently produce no changes in the rate of change of the framework density. Changes in linkage do, on the other hand, influence the packing of sodium; hence the breaks in the species density curve of sodium.

STRUCTURE-PHASE DIAGRAMS

The curves illustrated in Figs. 1-3 are essentially phase diagrams in that they reveal compositional regions where certain structural characteristics are predominant. The word "phase" is not used in the restricted sense that it has in physical chemistry. To avoid confusion, it is proposed to refer to the compositional regions as "structure-phases." From Fig. 2 one may deduce that the framework of sodium silicate glasses has two structure-phases, one above and one below the ratio .433. The latter is further subdivided into four subphases which are characterized by different packing laws of the sodium atoms. Similarly, it has been found in the potassium silicate system that the framework has only one structure-phase and that this is divided into a number of subphases.

The concept of structure-phases can be extended to three component systems, such as sodium potassium silicate, as well as two component ones. In this case it is not possible to plot the species density as a function of the silicon to oxygen ratio, since two abscissa are required, each of which is a measure of the effect of one metallic atom species. The ratios used for such three-dimensional diagrams are the ratios of each metal to oxygen. Actually, Figs. 1-3 might well have been plotted against the sodium to oxygen ratio. The resulting curves would have had the same appearance as when plotted against the silicon to oxygen ratio, since the two ratios are linearly related by the equation $\text{Na}/\text{O} = 2 - 4\text{Si}/\text{O}$.

The construction of species density diagrams can be accomplished with a minimum of experimental data, a fact which is of considerable value in the study

of glass systems. For the two component systems, each phase is represented by a straight line, and it is only necessary to determine the slope of the line. Given some background of knowledge of the system, two points may suffice for each phase. For three component systems, the phases are represented by planes, and in many cases three points may be sufficient.

APPLICATIONS OF THE SPECIES DENSITY ANALYSIS

Although the potential uses of structure-phase diagrams have not, as yet, been explored fully, it can be anticipated that applications will be found not only in the study of glass systems but also in such fields as mineralogy. Solid solutions in which one metallic species is progressively replaced by another might be analyzed for information as to the effect of size and charge of various species on structure. An interesting application is in systems containing atoms which take the silicon position at the center of the oxygen tetrahedron, as does aluminum. The structure in such cases is dependent, not on the silicon to oxygen ratio, but rather, on the silicon plus aluminum to oxygen ratio.

References

1. HUGGINS, M. L. *J. opt. Soc. Amer.*, 1940, **30**, 420.
2. MOREY, G. W. *The properties of glass*. New York: Reinhold, 1938. P. 237.

Mechanism of Spontaneous Cure in Puberty of Ringworm of the Scalp¹

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Since 1943 ringworm of the scalp hair caused by the fungus *Microsporon audouini* has been endemic among school children in numerous large cities of the United States (1). It has been known for more than 50 years (3) that although this infection is distressingly persistent during early childhood, it clears up spontaneously with oncoming adolescence. The scalp hair of adults is immune throughout life. For therapeutic purposes sex hormones have been administered to children with this disease in order to simulate pubertal conditions, but practicable doses have not been effective. From the therapeutic point of view it therefore seemed more promising to investigate the local changes on the scalp following puberty and to find out what makes the scalps of adults nonsusceptible to *M. audouini* infections. Such investigations were started a year and a half ago in the Division of

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Dermatology of the University of Chicago. It was learned (2) that there are ether-extractable substances on human hair that inhibit the growth of *M. audouini* on culture media. The total ether extract (hair fat) of adults was found to be five times as effective as the hair fat of children. This provided a ready explanation for the immunity of adults. Further confirmation was provided by the fact that 10 times higher concentrations of hair fat were required to inhibit the growth of certain other pathogenic fungi, such as *Trichophyton gypseum*, *Achorion schoenleinii*, and *M. lanosum*, to which the hair of adults is not immune.

In a search for the active fungistatic principle of hair fat it was found (2) that the neutral portion was quite inactive but that the free acidic components were strongly inhibitory. Further fractionation of the free fatty acids by steam distillation yielded a few per cent of a very potent material in the distillate, leaving the bulk of the free fatty acids as relatively inert residue. Acids above C_{12} are practically non-volatile with steam and have little inhibitory power. Vacuum distillation of the steam distillate yielded fractions, the activity of which decreased as the boiling point increased. The most active fractions, obtained in vanishingly small amounts, appeared on the basis of elementary analyses, molecular weight estimations, and qualitative reactions to be saturated monobasic acids in the range of C_7 to C_{11} . When added to Sabouraud's agar medium in graded amounts, these fractions completely inhibited the growth of *M. audouini* at concentrations of 0.0002 to 0.0005 per cent.

Experiments with all of the available monobasic aliphatic acids revealed that maximum fungistatic and fungicidal activity on *M. audouini* is possessed by the straight-chained saturated monobasic C_7 , C_9 , C_{11} , and C_{13} acids. These acids are the only ones which we have found to be comparable in activity to the most active fractions of hair fat.

Recently it has been possible to collect 45 kg. of adult hair, representing over 10,000 haircuts. Ether extraction was carried out in a 50-gallon tank and yielded 230 grams of free fatty acids along with several kilograms of neutral substances.

The free fatty acids were separated by careful fractional distillation of their methyl esters in a 100-plate still, operated at 2-mm. pressure. Chain lengths ranged from 7 to 22 carbon atoms. The C_7 to C_{11} fraction amounted to 1 per cent of the total and was refractionated in the presence of a mineral oil diluent in order to achieve more complete separation. Prominent in this fraction is pelargonic acid, the C_9 saturated normal aliphatic acid. Its identity has been confirmed by the melting point and nitrogen content of its amide. Not all of the component acids have

been identified. However, sufficient is known with certainty to report the presence of saturated and unsaturated normal aliphatic acids having both odd and even numbers of carbon atoms. Human hair fat appears to be unique among fatty materials, in that a whole series of normal aliphatic acids having odd numbers of carbon atoms is present in significant amount. The isolated acids containing odd numbers of carbon atoms are identical in fungistatic efficiency with the corresponding acids obtained from other sources.

Therapeutic experiments on hospitalized children with ringworm of the scalp were started early in this experimental work. Total hair fat, low-boiling fatty acid fractions from hair fat, pelargonic acid, and its equally fungicidal sodium salt were all applied in a variety of ways: by simple massage; by fixing the material to the lesions with air-tight dressings; in concentrated form and in varying dilutions; in combination with wetting agents; and by introduction of sodium pelargonate and sodium undecylenate into the hair follicles by means of galvanic current.

Unfortunately, no curative effect was obtained with any of our methods. *In vitro* experiments have shown the cause for these negative results: Neither the fatty acids nor their salts penetrate the keratin material of the hair, and therefore they are unable to exert their action on spores inside the hair. It seemed possible that the combination of a fungicidal fatty acid salt with a mild keratolytic agent such as sodium thioglycolate would facilitate penetration of the hair shaft, but the results so far have not been encouraging.

The failure of our therapeutic experiments led to the conclusion that, in nature, when the ringworm is healed during puberty, the fatty acids exert their fungicidal action by some means other than penetration of the hair. The fat, after it has been formed in the sebaceous glands, diffuses into the follicular canal, to the surface of the hair, and to the surface of the scalp. With oncoming adolescence the active fatty acids sterilize these pathways but not the hair shaft. However, when the infected hair falls out and a new hair is formed in the same follicle, this new hair is not infected because the inner surface of the follicle is sterilized. This situation results in cure when (after many months) all the infected hair has fallen out in the course of natural shedding. Correspondingly, the spontaneous cure in puberty is a rather slow process. Among our patients, children far advanced in puberty (girls menstruating for many months, boys with well-developed pubic hair) still had infected hairs. Although the mechanism of spontaneous cure seems to be well understood, a way to utilize this mechanism for a rapid cure has not been found, particularly because the generation change of hair in small children is slower than in puberty.

If a ringworm lesion is treated locally with pelargonic acid or other fungicidal agent, the spread of the lesion is checked immediately because the spread from one hair to another via follicular wall to surface of scalp, and from there into the inner follicular wall of the next hair and into the hair shaft, is inhibited. Hence, it can be concluded that local treatment of exposed but noninfected children, in schools, orphanages, and other places where children congregate in numbers, will effectively check the spread of epidemics. Whether such prevention is practicable has not yet been investigated.

Summary. With onset of puberty, the sebaceous glands of the scalp start to secrete a sebum which contains, in higher concentration than before, low-boiling saturated fatty acids with selective fungistatic and fungicidal action on *M. audouini*. Highly active normal aliphatic monobasic acids having odd numbers of carbon atoms, including pelargonic acid, have been isolated from hair fat of adults. The "adult type" of hair fat does not kill the fungus spores within the hair but prevents infection of the new hair following the old infected hair in the process of shedding.

Detailed reports are to be published elsewhere.

References

1. ROTHMAN, S. *Hygeia*, 1945, **23**, 436.
2. ROTHMAN, S., SMILJANIC, A. M., and SHAPIRO, A. L. *Proc. Soc. Biol. Med.*, 1946, **60**, 394.
3. SABOURAUD, S. *Ann. Inst. Pasteur*, 1895, **9**, 87.

Inhibition of the Catalyzed Thermal Decomposition of DDT

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Laboratory (2, 3, 4, 14) and field (2, 11) studies indicate that insecticidal preparations containing DDT may decompose thermally unless specifically protected from exposure to even moderately high temperatures. Evidence to the contrary has been published (1, 12, 13). Under field conditions, however, DDT as such may disappear so rapidly as to preclude mere evaporation (5) from consideration, particularly when a considerable residue of the almost noninsecticidal dehydrohalogenation product is demonstrable (10). The iron-catalyzed dehydrohalogenation of DDT has been amply verified (1, 2, 6-9). Because most technical DDT contains traces of iron or iron salts by the time it reaches the surface being treated, it seemed worth while to present this brief preliminary report upon two substances found to inhibit the iron-catalyzed thermal decomposition of DDT. The full details underlying this study will be reported elsewhere.

Picolinic acid (GD 2100)¹ and salicylal-amino-guanidine (GD 2101)¹ are the two inhibitory substances. When 1.5 per cent of ferric nitrate, 2 per cent of either inhibitor, and 96.5 per cent of iron-free technical DDT of setting point 90.1° C. were mixed intimately and heated 24 hours at 110-120° C., the resulting dehydrohalogenation was negligible (1.0 per cent for GD 2100; 2.5 per cent for GD 2101). Without inhibitor, the resulting dehydrohalogenation was complete under the same conditions. In Fig. 1 is

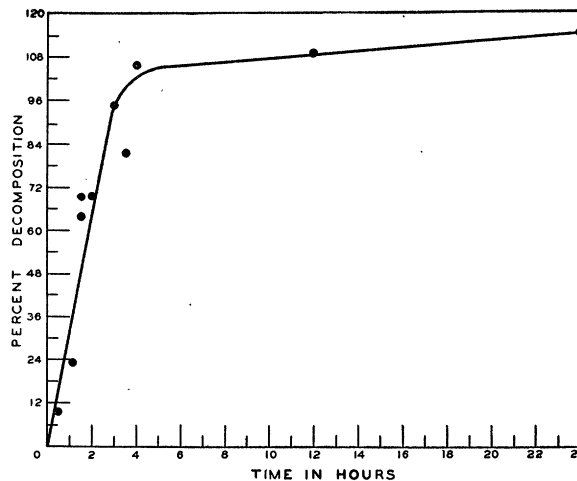


FIG. 1. Rate of decomposition (dehydrohalogenation) of technical DDT plus ferric ion as dehydrohalogenation catalyst at 110-120° C.

shown a plot of the rate of thermal dehydrohalogenation of the technical DDT plus ferric ion. The rate of dehydrohalogenation curves for similar mixtures plus the inhibitors, within the concentration range 2-20 per cent, were so nearly superimposable horizontal straight lines that they could not be plotted satisfactorily. Still lower concentrations of inhibitor may be equally effective, although this possibility has not been investigated.

That the inhibition of the iron-catalyzed thermal decomposition of DDT is not attributable solely to mere buffer action is evinced by extensive dehydrohalogenation in the presence both of calcium dihydrogen phosphate and of sodium carbonate. The effects of sunlight and weathering upon these two organic inhibitors are under investigation in field tests and will be reported elsewhere.

References

1. BALABAN, I. E., and SUTCLIFFE, F. K. *Nature, Lond.*, 1945, **155**, 755.
2. CHISHOLM, R. D. *U. S. Dept. Agric. Bull.*, E-643, March 1945.
3. CUTKOMP, L. K. Abstract of manuscript for publication, released by Committee on Medical Research and dated 19 April 1946.

¹ Covered by U. S. Patent 2,363,778 as metal deactivators and issued to C. J. Pedersen. Samples of these compounds were very generously supplied by H. C. Stecker, of E. I. du Pont de Nemours and Company, Wilmington, Delaware.