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Über die orientierte Aufwachsung von Polyäthylen auf Steinsalz

Über orientierte Aufwachsungen von hochpolymeren organischen Stoffen ist bisher nichts bekannt geworden. Nachdem es in neuerer Zeit gelungen ist, einerseits Einzelkristalle von linearem Polyäthylen herzustellen[1] und andererseits Kristalle der in ihrer Kristallstruktur dem Polyäthylen sehr ähnlichen[2] niedermolekularen Paraffine zur orientierten Aufwachsung auf Alkalihalogeniden zu bringen[3], bot sich das System lineares Polyäthylen – NaCl zur Prüfung der Frage, ob hochpolymere organische Stoffe orientiert aufzuwachsen vermögen, an.

Orientierte Aufwachsung von Polyäthylen auf (001) NaCl

Versuche mit einem linearen Polyäthylen (Marlex. M = 105 000) führten ohne weiteres zu den gesuchten Aufwachsungen. Das lineare Polyäthylen wurde aus einer 0,06prozentigen Lösung in Dekalin auf die Spaltfläche (001) eines auf 90° erhitzten Steinsalzkristalls aufgebracht. Das Polyäthylen orientierte sich auf (001) von NaCl in Nadeln mit der Nadellängsachse ‖ [110] und $[1\bar{1}0]$.

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Krefeld, Tiergartenstrasse 21, den 12. August 1957.

Summary

Orientated overgrowth of linear polyethylene on rocksalt is described. The needle-shaped crystals of polyethylene are orientated on (100) of NaCl with the long axe of the needles parallel to [110] and [110].

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[1] R. Jaccodine, Nature *176*, 305 (1955). – P. H. Till, Jr., J. Polymer Sci. *24*, 301 (1957).

[2] C. W. Bunn, Trans. Faraday Soc. *35*, 482 (1939).

[3] J. Willems, Naturwissenschaften *42*, 176 (1955).

On Chondroitin Sulphate and Mucoprotein from Cartilage

It has been proposed[1] that in mammalian hyaline cartilage chondroitin sulphate is present in two forms: about one third would be bound to a protein different from collagen to form a mucoprotein, the remainder being linked to collagen.

The present work was carried out on a product extracted from horse nasal septa cartilage. Aqueous solutions of 30% potassium chloride plus 1% potassium carbonate[2] were used in this extraction. After centrifuging, the extraction solutions were dialyzed and added with potassium acetate and alcohol at 0°C. The precipitates so obtained were redissolved and reprecipitated in a similar way and finally they were dried with absolute alcohol and ether.

The aim was to give a physicochemical picture of this product which will be referred to as MC.

The N content of MC (referred to the dry weight at 110°C) was 3·9%. Its amino acid composition, as revealed by paper chromatography, was as follows: aspartic acid, serine, glycine, glutamic acid, threonine, alanine, leucine (+++); ornithine, lysine, valine, phenylalanine (++); histidine, tyrosine, tryptophan, proline (+).

By paper electrophoresis (pH 2·0–10·0), it was found that MC was formed by two components. One was immobile and stained with light green and metachromatically with toluidine blue; the other one migrated towards the anode and only stained metachromatically with toluidine blue.

In the analytical ultracentrifuge, MC in phosphate buffer M/15, pH 7·0) exhibited a very diffuse and asymmetric boundary and it was impossible to obtain its sedimentation coefficient.

A light scattering study of MC in phosphate buffer as above made it possible to obtain the following values for the average molecular weight, dissymmetry, Z-average radius of gyration, respectively: $M_w = 1{\cdot}75 \cdot 10^6$; $z = 2{\cdot}05$; $R_z = 1100$ Å.

All the above results are easily explained if it is assumed that MC contains a certain amount of free polysaccharide besides the mucoprotein of high molecular weight. Owing to the relatively low molecular weight of chondroitin sulphate, the light scattering results must be referred to the mucoprotein. In this case too, using the

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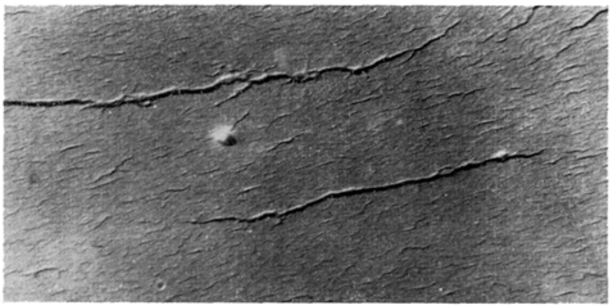
[1] J. Shatton and M. Schubert, J. biol. Chem. *211*, 565 (1954).

[2] J. Einbinder and M. Schubert, J. biol. Chem. *185*, 725 (1950).

same treatment of the Zimm plot as for a different mucoprotein preparation previously studied[3] (according to the papers of SADRON and BENOIT[4], and BENOIT[5]), it is possible to conclude that a polydisperse system of coils is the best model for the molecular shape of MC in salt solution.



Electron micrograph of MC ($1 \cdot 10^{-5}$ g/ml in distilled water). Magnification: 30000 ×. Shadowing with gold-manganine at 20°.

An investigation with the electron microscope of extremely dilute aqueous solutions of MC showed the presence of fibrous structures (Figure). These fibres are thought to be formed by side aggregation of smaller units, possibly of mucoprotein and chondroitin sulphate molecules. They seem to confirm: (*a*) the previously postulated end-to-end arrangement of polysaccharide and polypeptides in the mucoprotein molecules[6], and (*b*) the suggested possibility of linkages between acid groupings of chondroitin sulphate or mucoprotein molecules and basic groupings of other mucoprotein molecules when the ionic strength of the medium is very low and consequently the ionization is high[7].

A more detailed account of this work will be published in due course elsewhere.

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Riassunto

Sono riferiti i risultati di uno studio chimico-fisico sul condroitinsolfato e sulla mucoproteina della cartilagine. È brevemente discusso il significato di questi risultati in relazione ad una struttura precedentemente proposta per la mucoproteina.

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[3] G. BERNARDI, Nature *180*, 93 (1957).

[4] C. SADRON, H. BENOIT, M. DAUNE, Int. Symp. macromol. Chem. (Milan-Turin, 1954).

[5] H. BENOIT, J. Polym. Sci. *11*, 507 (1953).

[6] G. BERNARDI, Biochim. biophys. Acta (in press).

[7] G. BERNARDI, C. r. Acad. Sci. *244*, 1918 (1957).

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The Structures of Ambrosin and Damsin[1]

Two crystalline compounds, named ambrosin and damsin, have recently been isolated from *Ambrosia maritima* L., fam. Compositae, by ABU-SHADY and SOINE[2]. The same authors carried out a thorough study of the oxidation and reduction of the two natural products and the following conclusions were made at that time. Ambrosin and damsin contain the same carbon skeleton and are tricyclic. The formation of an unidentified azulene on dehydrogenation of 'reduced ambrosin' suggested the presence of a substituted bicyclo-(5,3,0)-decane skeleton in these two natural substances. Finally the authors suspected a structural relation between ambrosin and helenalin.

Recent work on helenalin has shown that this sesquiterpene lactone is represented by I[3]. We have now used the information gained from the study of both helenalin (I) and tenulin[4] (III) to deduce possible structures for ambrosin and damsin.

The azulene obtained previously[2] was characterized by a trinitrobenzene-adduct, m.p. 125–130°, and in our opinion represents the derivative of chamazulene (IV), m.p. 132°[5]. This finding suggests that ambrosin and damsin belong to the guaianolides, a group of sesquiterpenes which are known to occur frequently in plants of the Compositae family.

The ultraviolet absorption spectrum of ambrosin (λ_{max} 217 mμ, ε 13465) cannot be reconciled with the presence of a cyclopentenone chromophore alone, because such systems are characterized by low extinctions. (Dihydrohelenalin V has λ_{max} 227 mμ, ε 7250 and tenulin III has λ_{max} 226 mμ, ε 7000.) The light absorption must therefore be due to two isolated chromophores and like in helenalin (I) (λ_{max} 220 mμ, ε 12200), the terminal methylene group in ambrosin must be conjugated with the γ-lactone ring. The second chromophore should therefore absorb like dihydrohelenalin (V) and we can conclude that ambrosin is in fact an α- or β-substituted cyclopentenone. The ready formation of bromoambrosin and particularly its light absorption (λ_{max} 248 mμ, ε 7025) strongly suggests that it is a α-bromo-β-alkyl cyclopentenone[6] and ambrosin, therefore, is a β-alkylcyclopentenone. The evidence discussed thus far can be summarized in the partial symbols IX and X.

There is no conclusive evidence at hand which would allow a distinction between the two alternatives IX and X. However, tenulin (III), helenalin (I) and geigerin[7], all isolated from Compositae, have been shown to be C_2-ketones rather than C_3-ketones and we would like to suggest, on biogenetic grounds, that ambrosin and damsin contain part structure IX.

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[1] Terpenes VIII. Part. VII, G. BÜCHI and W. S. SAARI, J. Amer. chem. Soc. (in press).

[2] H. ABU-SHADY and T. O. SOINE, J. Amer. pharm. Ass. *42*, 387 (1953); *43*, 365 (1954).

[3] G. BÜCHI and D. ROSENTHAL, J. Amer. chem. Soc. *78*, 3860 (1956). – V. HEROUT, M. ROMANUK, and F. SORM, Coll. Czechosl. chem. Comm. *21*, 1359 (1956). – R. ADAMS and W. HERZ, J. Amer. chem. Soc. *71*, 2456, 2551, 2554 (1949).

[4] D. H. R. BARTON and P. DE MAYO, J. chem. Soc, *1956*, 142.

[5] A. MEISELS and A. WEIZMANN, J. Amer. chem. Soc. *75*, 3865 (1953). – F. SORM, J. NOVAK, and V. HEROUT, Coll. Czechosl. chem. Comm. *18*, 527 (1953).

[6] A. L. NUSSBAUM, O. MANCERA, R. DANIELS, G. ROSENKRANZ, and C. DJERASSI, J. Amer. chem. Soc. *73*, 3263 (1951). Bromohelenalin has λ_{max} 248 mμ, ε 6300; R. ADAMS and W. HERZ, J. Amer. chem. Soc. *71*, 2456, 2551, 2554 (1949).

[7] G. W. PEROLD, J. chem. Soc. *1957*, 47.