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The Rheochor and Hydrogen Bond Structure of Polyfunctional Alcohols in Binary Mixtures with Dimethyl Sulphoxide

Kaj Hästbacka and J. Johan Lindberg

Department of Chemistry, University of Helsingfors, Finland

In recent times dimethyl sulphoxide (DMSO) has been used as a solvent for various polymeric hydroxylic compounds such as e. g. lignins, xylans and sugars and cellulose derivatives[1] From the point of view of the mechanism of the solvation of these systems it would be of interest to investigate the relation between hydrogen bond formation and the rheological behaviour in binary mixtures containing DMSO and polyhydroxylic alcohols. Owing to the lack of an adequate theory for the structure of strongly associated liquid mixtures, the empirical approach seems still to be the most effective one when treating the problem on the relation between structure and viscosity in hydrogen bonded systems.

Thus, in a previous report[2] the rheochor concept of Friend and Hargreaves[3] was used to describe the relation between structural and viscosimetric behaviour of binary mixtures. Furthermore an excess rheochor, $[R]_\eta^E$,

$$(1) \qquad [R]_\eta^E = [R]_\eta^M - [R]_\eta^{id}$$

was defined to allow for the deviation from ideal behaviour. The indices E, M and id in eq. 1. refer to the excess function, the actual and the ideal mixture respectively.

The viscosity and excess rheochor curves show the same trends in general. In certain cases, however, the structural effects are more pronounced and more easily observed when using the latter function. In addition, owing to the constitutive additivity of the rheochor (in the same manner as for refractivity, molar volume and parachor) this function is more directly related to the anomalies caused by the hydrogen bond formation on the molecules, than the viscosity itself.

A comparison of the excess rheochors of various binary mixtures (cf. e. g.[2] and the references quoted there) seems to indicate that low-molecular mono-hydroxylic alcohols and also dimethyl sulphoxide often have a diminishing effect on the excess rheochor. This effect seems to increase further with increasing length of the aliphatic side chain of the alcohol. On the contrary, water, acetic acid and chloroform seem to increase the excess rheochor. Although there does not seem to be any quite simple relationship between these effects and other physico-chemical constants, some correlation with internal pressure, heat of mixing and dielectric relaxation time is deductable as stated in a previous report[4]. In order to elucidate these findings and to study further the effect of chain branching and polyfunctionality on viscosity and excess rheochor the results of measurements on binary mixtures containing DMSO and 1,2,3-propanetriol, 1,2-ethanediol or 2-methoxyethanol will be reported in the present paper.

Experimental. The viscosities and densities were determined at 25°, 35° and 45°C using Ostwald viscosimeters and pycnometers in the previously described manner [2,5]. In the case of the system DMSO-1, 2, 3-propanetriol the points of highest viscosity were measured using a Höppler viscosimeter. The calculations of the results were performed using the viscosity values of carefully purified 1, 2, 3-propanetriol, DMSO, water and CCl_4 as points of reference. Contamination with air humidity was carefully avoided during the measurements and storage of the reagents.

Reagents. The reagents were purified from commercial materials by anhydridization, distillation and recrystallization to give physical constants (density, refractive index, boiling and melting points) in accordance with data for the purest possible compounds as reported in the litterature[6]. Some of the methods of purification will be discussed below..

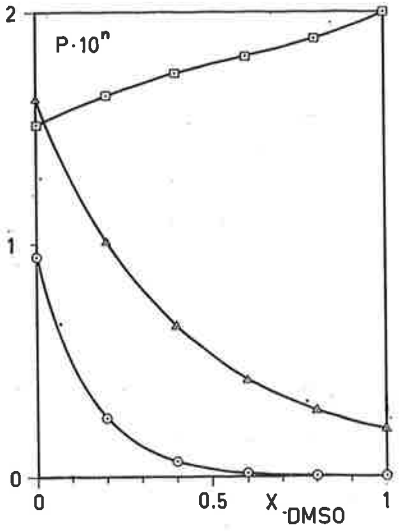

Fig. 1. Viscosities of binary mixtures at 25°C DMSO-1, 2, 3-propanetriol, cP.10^{-2} —⊙—⊙—⊙—, DMSO-1, 2-ethanediol, cP.10^{-1} —△—△—△—, DMSO-2-methoxyethanol, cP —⊡—⊡—⊡—.

Results. The results of the measurements and calculations of molar volumes, viscosities, enthalpies of viscous flow and rheochors at 25°, 35° and 45°C are collected in Tables 1—4 for the systems DMSO—1,2,3-propanetriol, DMSO-1,2-ethanediol and DMSO-2-methoxyethanol. In Figures 1—4 the viscosities at 25°, 35° and 45°C, the excess rheochors at 25° and excess molar volumes and relative excess molar volumes at 25° and excess molar volumes and relative excess molar volumes at 25°C are depicted as a function of molar composition for the mentioned systems.

Fordham[8] found that the viscosity as a function of the temperature for 1,2-ethanediol can be represented between 25—50°C by the equation

$$(2) \qquad \log_{10} = -3.7830 + 1494/T$$

where T is the absolute temperature. Recalculated to the temperatures 25°, 35° and 45°C it corresponds to the viscosities 17.0, 11.7 and 8.2 cP respectively. On the other hand Timmermanns and Hennaut-Roland[9] found the values $\eta^{15} = 26.09$ and $\eta^{30} = 13.55$ cP respectively. By distilling commercial 1,2-ethanediol twice at atmospheric pressure through a Wigreux column of 40 cm length with careful exclusion of the humidity we obtained a product with the viscosity value $\eta^{25} = 16.25$ cP. If the same commercial product was distilled through the

Table 1. Densities, Molar Volumes and Viscosities of the Binary System DMSO-1, 2, 3-Propanetriol at 25°, 35° and 45°C.

X_{DMSO}	v^{25} cm^3	d_4^{25}	η^{25} cP	d_4^{35}	η^{35} cP	d_4^{45}	η^{45} cP
0.00	73.20	1.2581	945.0	1.2521	410	1.2457	215
20	72.54	1.2310	253.5	1.2243	127.1	1.2170	71.78
40	72.03	1.2010	68.08	1.1930	39.45	1.1859	24.15
60	71.65	1.1685	19.05	1.1606	12.47	1.1523	8.590
80	71.41	1.1332	5.754	1.1246	4.217	1.1157	3.258
1.00	71.30	1.0958	2.000	1.0859	1.659	1.0757	1.395

Table 2. Densities, Molar Volumes and Viscosities of the Binary System DMSO-1, 2-Ethanediol at 25°, 35° and 45°C.

X_{DMSO}	v^{25} cm^3	d_4^{25}	η^{26} cP	d_4^{35}	η^{35} cP	d_4^{45}	η^{45} cP
0.00	55.93	1.1098	16.92	1.1034	11.45	1.0958	8.057
20	58.87	1.1090	10.64	1.1016	7.439	1.0938	5.541
40	61.87	1.1070	6.847	1.0991	4.943	1.0905	3.883
60	64.95	1.1041	4.431	1.0954	3.422	1.0863	2.753
80	68.09	1.1003	2.996	1.0910	2.370	1.0815	1.953
1.00	71.30	1.0958	2.000	1.0859	1.659	1.0757	1.395

Table 3. Densities, Molar Volumes and Viscosities of the Binary System DMSO-2-Methoxyethanol at 25°, 35° and 45°C.

X_{DMSO}	v^{25} cm^3	d_4^{25}	η^{25} cP	d_4^{35}	η^{35} cP	d_4^{45}	η^{45} cP
0.00	79.24	0.9604	1.515	0.9512	1.251	0.9417	1.045
20	77.48	0.9875	1.641	0.9783	1.358	0.9689	1.143
40	75.06	1.0140	1.733	1.0047	1.439	0.9952	1.211
60	74.28	1.0408	1.809	1.0312	1.507	1.0215	1.269
80	72.78	1.0681	1.884	1.0582	1.567	1.0483	1.318
1.00	71.30	1.0958	2.000	1.0859	1.659	1.0757	1.395

Table 4. Enthalpies of Viscous Flow Calculated according to the Eyring Equation[7], ΔH_v and Mixture Rheochors, $[R]\,{}^{M}_{\eta}$ at 25°C for the Systems DMSO-1, 2, 3-Propanetriol, DMSO-1, 2,-Ethanediol and DMSO-2-Methoxyethanol. The ΔH_v-values are given in kcal/mole units and the $[R]\,{}^{M}_{\eta}$ in cgs-units.

X_{DMSO}	1, 2, 3-Propanetriol		1, 2-Ethanediol		2-Methoxyethanol	
	ΔH_v	$[R]\,{}^{M}_{\eta}$	ΔH_v	$[R]\,{}^{M}_{\eta}$	ΔH_v	$[R]\,{}^{M}_{\eta}$
0.00	18.0	96.92	7.3	44.36	3.5	46.93
20	13.7	81.47	7.0	44.21	3.5	46.35
40	10.2	68.65	6.6	43.93	3.4	45.69
60	8.2	58.29	4.7	43.65	3.4	44.99
80	6.0	49.99	4.5	43.65	3.4	44.30
1.00	3.4	43.72	3.4	43.72	3.4	43.72

same column in a vacuum (8 mm Hg), dried overnight with Drierite and redistilled at the same reduced pressure, all operations being performed with the exclusion of humidity, a viscosity value of $\eta^{25} = 16.92$ cP was obtained (cf. also Table 2 for the corresponding data at other temperatures).

A graphic comparison of the different data reveals that our latter values are in closer agreement with those of Fordham than with those of Timmermanns and Hennaut-Roland. Moreower as could be expected, owing to the strong adherence of water to 1,2-ethanediol, the latter product is obtained as more anhydrous than the former; the results obtained with it were therefore used as a basis for the calculations.

In the case of 2-methoxyethanol by drying and destillating three times through a 40 cm Wigreux column of the commercial sample at athmospheric pressure and with exclusion of humidity a product was obtained which shoved a viscosity $\eta^{25} = 1.515$ cP differeng somewhat from previously reported data ie. 1.60 cP[10]. However, owing to the lack of knowledge regarding the method of purification and purity of the substance in the mentioned case, our own value was preferred and no further purification was attempted.

In this connection it is worth while mentioning that for all compounds investigated here our values of densities and boiling or melting points agreed within the limits of experimental error with those given in the litterature [6].

Discussion. A study of the data in the tables and the figures shows some remarcable facts. Thus in the case of the systems DMSO-1,2,3-propanetriol and DMSO-1,2,-ethanediol small amounts of DMSO already bring out a very rapid decrease in viscosity, whereas in the case of DMSO-2-methoxyethanol the influence of DMSO is very small. It seems evident therefore, that in the two former cases DMSO is extensively breaking up the three-dimensional hydrogen bond structure and causing an effect similar to that observed for binary systems containing DMSO and simple monohydroxylic alcohols.[2] Furthermore the excess rheochors of the systems DMSO-1,2-ethanediol and DMSO-2-methoxyethanol are only very weakly negative as compared to the systems DMSO-monohydroxylic alcohols and especially DMSO-1,2,3-propanetriol. It seems that the anomalies observed can be largely explained in terms of a definite compound formation, probably of 1:1 type between DMSO and the hydroxylic compound.

If the theory proposed by Suryanarayana [11] is correct that the viscosity, molar volume and dielectric constant of a mixture are functions of the internal pressure; the same trends should be observed in the excess rheochors, excess molar volumes and excess dielectric constants (cf. for its definition ref.[12]). The

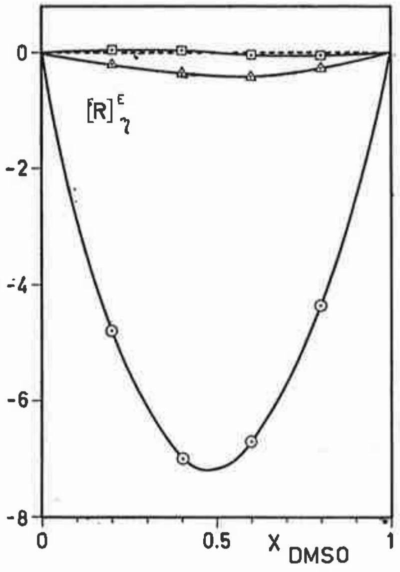

Fig. 2. Excess rheochors of binary mixtures at 25°C. The curves are denoted as in Fig. 1.

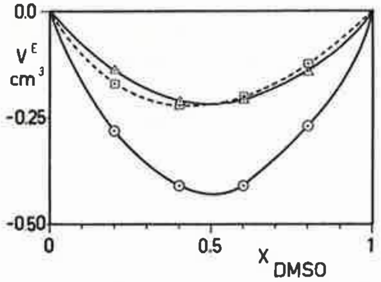

Fig. 3. Excess molar volumes of binary mixtures at 25°C. The curves are denoted as in Fig. 1.

graphs given in Fig. 1 and 3 reproduce the excess rheochors and excess molar volumes of the investigated systems and seem to some extent to support the indicated theory. This is especially evident if as given in Fig. 4, the excess molar volume is divided by the molar volume itself, ie. V^E/V is plotted as a function of molar composition.

It was previously found [2] that the enthalpy of viscous flow of DMSO is of the same magnitude as that of the simple alcohols and water, whereas, as can be seen from Table 4 of the present paper, it is much smaller than that of 1,2,3-propanetriol and 1,2-ethanediol, but equal to that of 2-methoxyethanol. It has been shown previously that the pronounced association

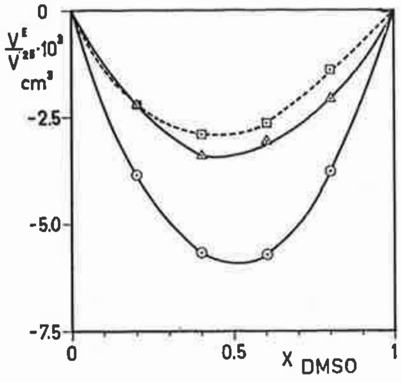

Fig. 4. Excess molar volume divided by molar volume for binary mixtures. The curves are denoted as in Fig. 1.

of DMSO should primarily be of the chain type.[13] The above mentioned effects are quite explicable in terms of these findings.

Acknowledgement. One of the authors (L) acknowledges, his indebtedness to the Finnish Society for Sciences and the State Board of Science for financial aid.

Summary

The viscosities and densities at 25°, 35° and 45°C have been determined for the systems dimethyl sulphoxide- 1, 2, 3-propanetriol, -1, 2-ethanediol and -2-methoxy ethanol in the whole range of concentrations. The structure of the associates formed has been discussed in terms of the excess rheochor, excess molar volume, enthalpy of viscous flow and internal pressure of the systems.

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Synthesis and Labelling of Carotenes* and Carotenoids

R. Morf

I. Introduction

The constitution of the two hydro-carbons beta-carotene and lycopene and of the hydroxy derivative zeaxanthene were made exactly 30 years ago. The total synthesis of Vitamin A was achieved in 1946. In the seventeen years many attempts were made in order to synthesize the more important representatives of the carotenoids. In 1950 Karrer in Zurich and Inhoffen in Germany were simultaneously successful in the total synthesis of beta-carotene. Five years later in 1955, it was possible taking advantage of the above mentioned first syntheis to achieve an industrial synthesis of this beautiful dye-stuff. Following this first technical synthesis, great efforts were made by various groups — I mention Inhoffen, Karrer, Pommer and Weedon — and also in Basle, to extend this synthesis to other important representatives in this interesting group of natural products.

The interest in this group emanates from the fact that many carotenoids have some vitamin activity. They are part of our daily food and they are transferred in the animal into Vitamin A itself.

Carotenoids which are suitably labelled by radioactive carbon are an important tool for the Biochemist. The metabolism and the conversion of carotene into Vitamin A can be studied with the help of labelled carotenoids.

In the first part of my talk, I make a survey in which the procedure of synthesis is explained. In the second part I shall enter into some detail telling of the problems of synthesis of intermediate products. In these details, you will see where there are possibilities of labelling.

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* Lecture given 11th March 1963 by invitation of Suomen Kemistien Valtuuskunta-Centralrådet för Finlands Kemister.

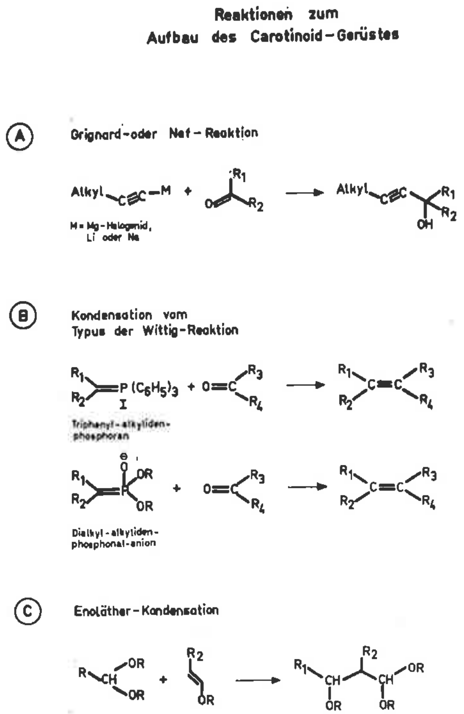


Fig. 1.

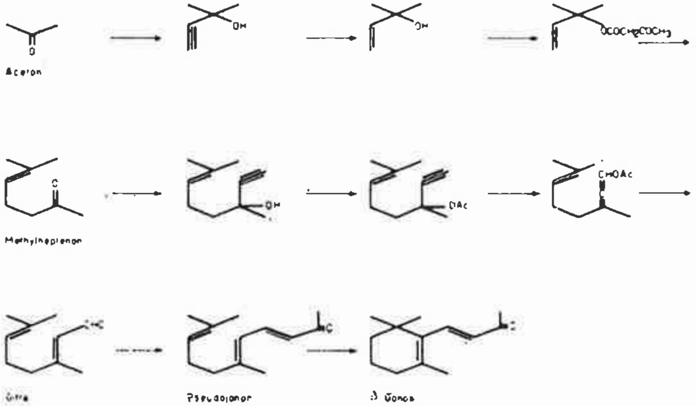
In the synthesis of the hydrocarbon beta-carotene itself which contains 40 carbon atoms, it has proved easier if two aldehydes of 19 carbon atoms each are reacted with acetylene. This type of reaction the well-known Grignard, is shown in principle in Figure 1 (A).

Another procedure has been discovered and very well interpreted by Wittig in Germany, it is listed under (B) in Figure 1. The condensation of carbonyl with phosphoranes, phosphonate-aniones.

Finally, under Figure 1 (C), a very useful reaction is demonstrated in which acetales with enolethers are reacted under catylical action on zinc chloride or bortrifluoride.

II. Starting material

Many syntheses of carotens and in particular the industrial procedure are based on citrale, beta-ionone and beta-carbon 19-aldehyde. As everybody knows beta-ionone is a well-known perfume which was found in violets and which was for the first time synthesized at the beginning of the century. Beta-ionone



β-Jonon aus Aceton

Fig. 2.

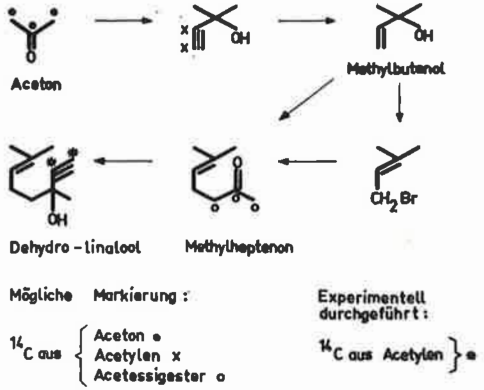
is still now synthesized sometimes by the old method from lemongrass oil which contains 75 % aldehyde, but the bulk of beta-ionone nowadays is fully synthesized starting with acetone and acetylene.

The total synthesis of beta-ionone goes from acetone to methylbutinol to methylbutenol. Condensation with dicetene and pyrolysis of the resulting aceto-acetate gives methylheptenone. Then follows an addition of acetylene in liquified ammonia as a medium. The resulting dehydrolinalool is acetylated. The acetate is converted into the alleneacetate by heating in acetic acid in the presence of silver catalyst. Saponification leads to citral. The well-known condensation with acetone gives pseudo ionone. Cyclisation results in beta-ionone.

From what I have told and shown you it is easily understood that there is now the possiblity that the beta-ionone ring be labelled wherever you like. If, in the synthesis, you start with labelled acetone the label will be at the C-atom No. 1. If, however, you start with labelled acetylene you get the labelled carbon-atom at one of the places of the acetylene. If you prefer to have a label later in the skeleton it is necessary to utilise labelled aceto-acetate. It is obvious when labelling such a complicated compound that the best and cheapest result is obtained when labelling is done towards the end of the synthesis.

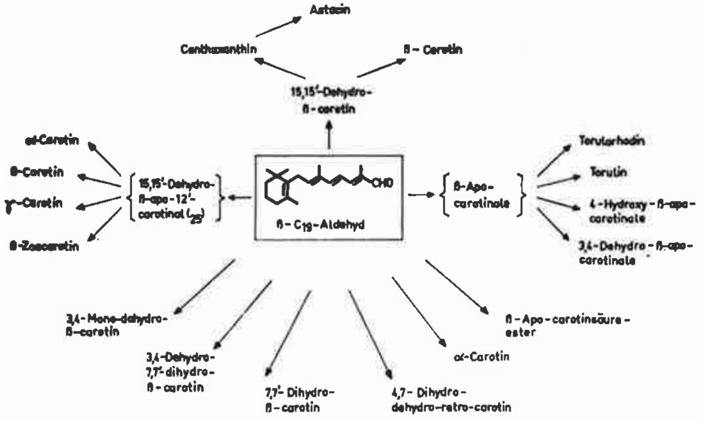
In the following picture you will always see the labelled carbon atoms indicated by an asterisk.

In Figure 4 you see the most important intermediate product the betacarbon 19 aldehyde. This aldehyde is synthesised from citral via beta-ionone and dehydrolinalool. This aldehyde



Dehydrolinalool aus Aceton

Fig. 3.



Synthetische Carotinoide aus ß-C19-Aldehyd

Fig. 4.

does not possess a full chain of conjugated double bonds. There is one interruption by a CH_2 group. From the many syntheses made out of this very important intermediate I should like to mention only a few which are technically important namely:

beta-carotene
canthaxanthene
astacene
beta-apocarotenale
Apocarotenic acid and its ester
Torularhodine

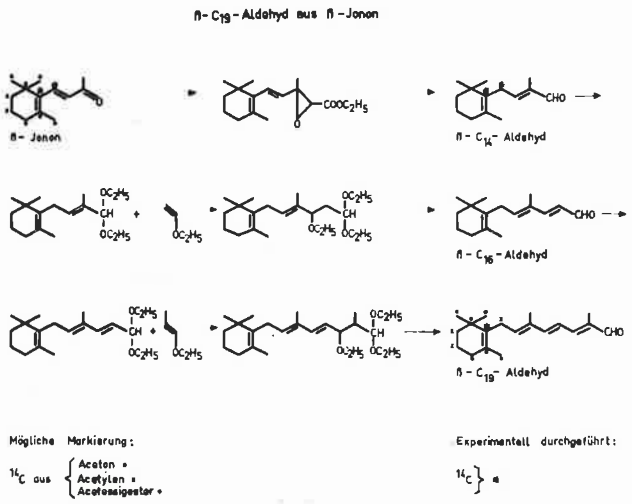


Fig. 5.

Starting form an aldehyde with 25 carbon atoms we made the synthesis of beta and gama carotene.

The technical synthesis of this importatnt C_{19}/-aldehyde is given in detail. The first step of this synthesis, namely from ionone to the 14-aldehyde, is achieved by glycidic ester synthesis in a very good yield. The prolongation of the carbon atom chain by two carbon atoms is achieved by enol-ether condensation. The resulting 16-aldehyde is again reacted with propinyl-ether which results un the above-mentioned 19-aldehyde.

Beta-Carotene is the most important representative of the carotenoids. Moreover, it is an important natural source of Vitamin A_1, so-called pro-Vitamin A. Knowing of the composition and the structure of these two compounds the vitamin-activity of bety-carotene is easily understood.

Fig. 6.

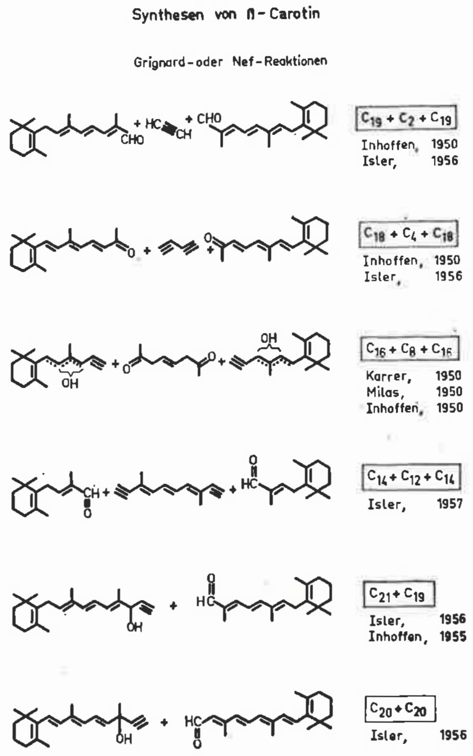


Fig. 7.

Slide No. 6 shows you one single carotene-crystal which was photographed by our colleague Dr. Waldmann in polarized light.

The great scientific and technical interest towards carotene is demonstrated by the many attempts and efforts for its synthesis.

There exist more than 20 original papers which describe the great variety in the possible synthesis of carotene. In Figure No. 7 we look at those syntheses which utilize either the Grignard or the Nef reactions.

The first four proposals have each a symmetrical compound in the centre of the molecule which is on both its ends attached to one end the same ionone-ring-derivative. The first synthesis was by Inhoffen in 1950 and this was elaborated in 1956 by Isler. This is shown in the upper line of Slide No.7 They utilized acetylene as a centre component, which is condensed on both ends with one aldehyde C19. These syntheses will later be described in more detail.

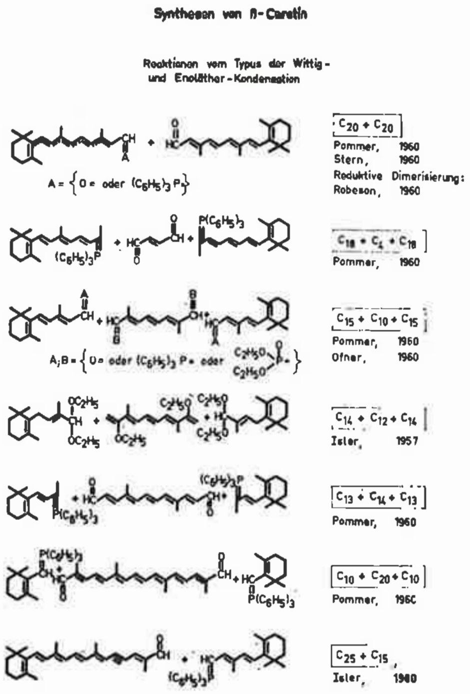


Fig. 8.

Another synthesis — also from Inhoffen — starts with diacetylene in the centre and two C_{18} cetones on both ends.

A third synthesis described by Karrer as well as by Inhoffen and Milas, untilizes octene-dion in the centre and two molecules of a C_{16}-Acetylene-compound. Isler in Basle was able to synthesis a very specific di-cis-11-11′ beta-carotene when two beta-C_{14} aldehydes were coupled with one molecule of C_{12}-diacetylene-hydrocarbon.

When the labelled atom must be attached to acetylene it is most convenient to convert the C_{19} aldehyde into the C_{21} acetylene-carbinol which will be condensed at a later stage with another C_{19} aldehyde.

The last proposal finally utilizes the principal $C_{20} + C_{20} = C_{40}$ which means one molecule of Vitamin A-aldehyde reacts with one molecule of the acetylenecarbinol of C_{18} acetone.

We now come to the Wittig reaction which is the basic principle for another 7 synthetic ways: Pommer on the simple formula $C_{20} + C_{20} = {}_{40}$ reacted Vitamin A-aldehyde with the phosphorane from Vitamin A. Stern made a slight variation by changing over

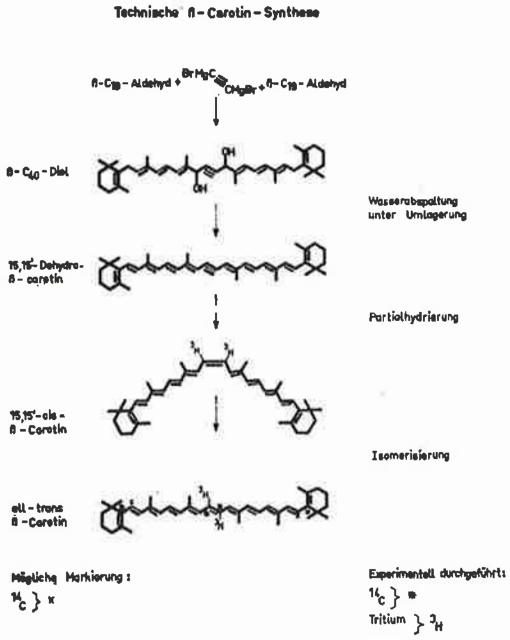


Fig. 9.

to one isomer of Vitamin A. Very interesting is the proposal of Dimerization of Vitamin A-aldehyde with the reducing agent P_2 S_5 (phosphor penta sulphide).

Pommer — in another Wittig reaction — reacted C_4-dialdehyde with two molecules of C_{18} phosphoranes. Also he tried oneC_{10} aldehyde with two C_{15} phosphoranes.

Isler in Basle starting with two molecules of C_{14} Acetale utilized the enolether condensation with C_{12}-dienolether. This very efficient vay was also successful when synthesizing zeaxanthene. C_{14}di-aldehyde was attached on both ends to C_{13}-phosphoranes.

Finally the combination of C_{25} aldehyde with the phosphorane from C_{15} gave a successful approach to gama and beta-zeaxanthene.

Having shown so many varieties it is now my plaesure to tell in more detail how beta-carotene since 1955 is actually made in Basle.

As you will see in this slide, we start with the simplest C_2 compound Acetylene which is converted on both ends into its Grignard-component,

These are reacted with two molecules of C_{19} Aldehyde. The result is a C_{40}-diol.

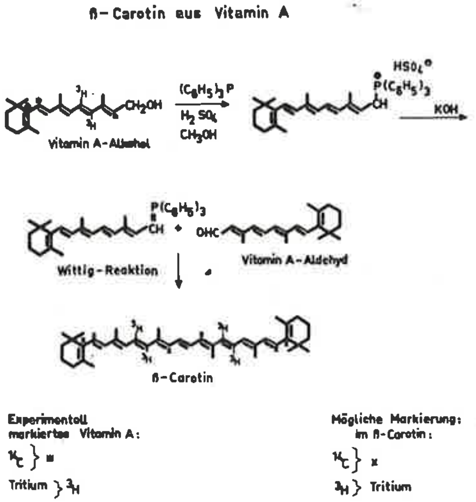


Fig. 10.

Water is drawn off from this diol by treatment with acid. The allylic rearrangement which follows gives an hydrocarbon containing all the 40 carbon-atoms of beta-carotene but which has an acetylenic bond in the centre. This hydrocarbon is characterized by a good tendency of crystallization. Purification therefore is done at this stage.

The triple bond in the centre is hydrogenated into the double bond with Lindlar catalyst under special conditions.

We obtain 15—15′ cis beta-carotene which can be rearranged into all-trans-beta-carotene.

The last hydrogenation process gives a good opportunity for labelling at the C_{15} position when we apply a hydrogen gas containing a certain amount of tritium. This was done by Dr. Würsch.

III. Lycopene and xanthophylls

Having spent much time in the description of carotene itself, I should now like to give you a short survey on the work done with the aim of synthesizing some of the more important yellow dye-stuffs which occur in nature. I start with lycopene, the dye-stuff from tomatoes. Lycopene has the same Brutto formula as carotene C_{40} H_{56} but has 13 conjugated double-bonds and, therefore, absorbs the light at longer wave-lengths than carotene. Also it cannot have any iononic rings. Slide No. 11 from "camera" shows you crystals of lycopene. The solution of lycopene in oil is a beautiful red.

Fig. 11.

The synthesis of lycopene was first described by Karrer in Zurich.

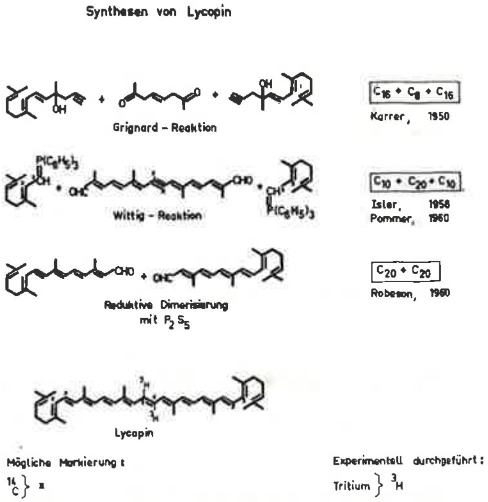


Fig. 12.

The principle of Karrer's synthesis is based on a double Grignard-Reaction with the components $C_{16} + C_8 + C_{16} = C_{40}$

There is a more efficient synthesis in which the Wittig Reaction is applied $C_{10} + C_{20} + C_{10} = C_{40}$ namely, geranglphosphorane is condensed with the dialdehyde of crocetene. Dr. Würsch in Basle labelled synthetic lycopene with tritium in the centre of the molecule.

If you want to label with carbon fourteen this might be best achieved in the two 6—7 positions.

Fig. 13.

IV. Cetones, Aldehydes etc.

We come now to the oxygenated and hydroxy carotenoids.

Canthaxanthene.

Canthaxanthane has two ceto-groups on each of the iononerings. In nature it occurs in the feathers, heart and liver of birds and in mushrooms. Owing to the two ceto-groups, conjugated with the system of double-bonds canthaxanthene gives beautiful deep red shades. Three different ways of synthesizing have been successful.

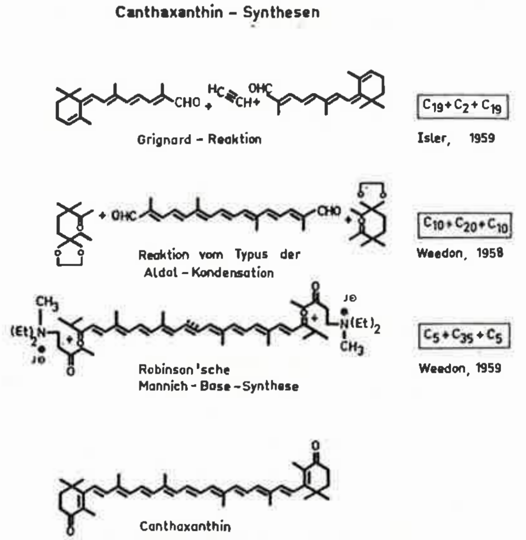


Fig. 14.

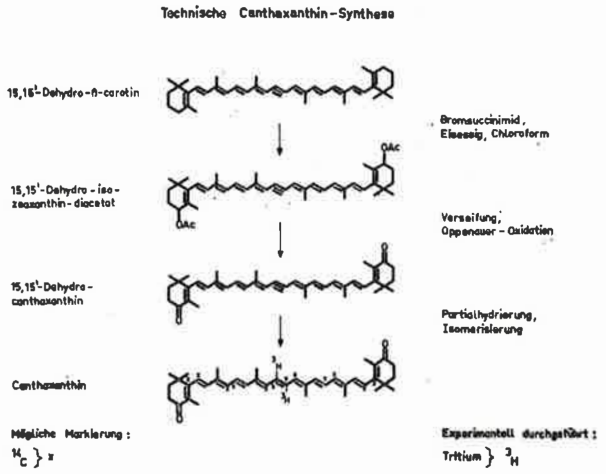


Fig. 15.

The first synthesis was based on the formula
$C_{19} - C_2 - C_{19} = C_{40}$

Acetylene was reacted with Grignard and two molecules of retro-C_{19}aldehyde. Weedon 1958 started from crocetene-dialdehyde which in a double Aldol-condensation reacted with C_{10}-Methylcetone. The technical synthesis is shown in Slide 15.

For the technical synthesis advantage was taken from an intermediate compound of the carotene-synthesis. The dehydro beta-carotene. With bromosuccineimide in acetic acid we get the diacetate of the dehydro-isozeaxanthene.

The resulting acetylenic compound is partially hydrogenated and finally isomerized to the all-trans canthaxanthene.

With regard to labelling it would be possible to apply exactly the same procedure as utilized with carotene. Würsch made the tritium compound.

There have been many successful syntheses made of various ceto and hydroxy carotenoids but I believe it would be too tiresome to mention all this very skilful puzzling work.

Before coming to my concluding remarks, let me shortly tell you how in the laboratory one was able to synthesise astacene, the red dyestuff of the boiled lobster. Astacene is a tetraceto-beta-carotene.

The starting material is canthaxanthene as described before. Weedon showed that by oxydation with oxygen in the presence of potassium-tertiary butylate, two additional ceto-groups can be formed.

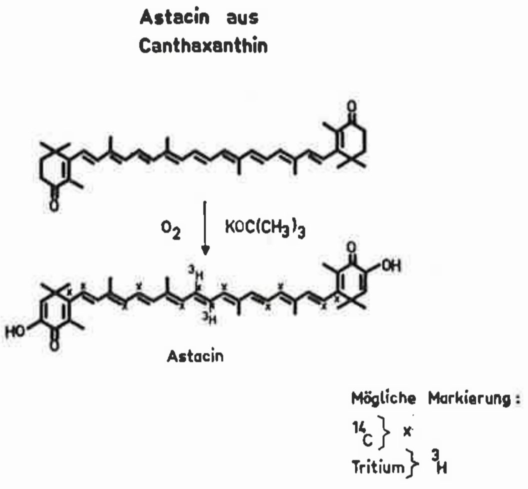


Fig. 16.

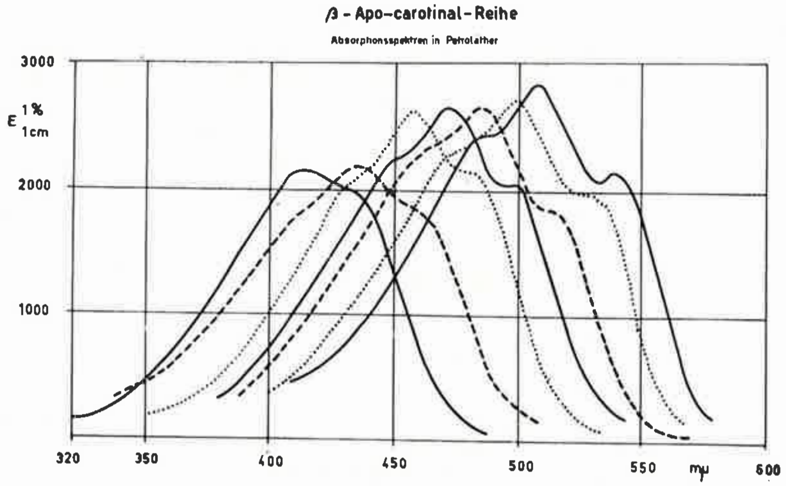


Fig. 17.

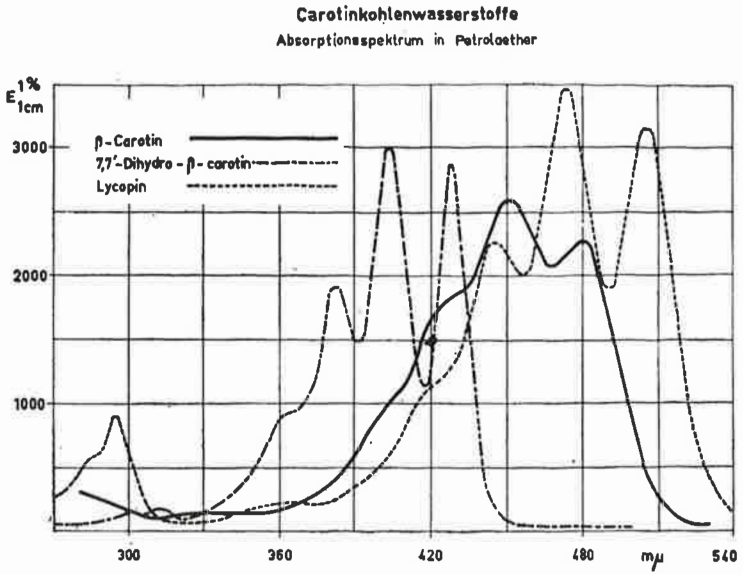


Fig. 18.

Two of the ceto-groups on both ends of the molecule seem to be in the enolic form which explains the deep red colour in the oily solution.

In conclusion, I should like to show you a few slides which explain clearly how the absorption-spectra change towards longer wavelengths in the function of the number of conjugated doublebonds or other chromoforic groups occur.

The synthesis of so many natural carotenoids is not only very exciting in view of getting a complete palette of beautiful shades, but the unique opportunity of labelling these compounds with tracers opens to the biologist a very promising future outlook.

I wish to thank all those whose untiring efforts have made this talk possible, amongst whom I would like to mention Dr. Otto Isler, Dr. Lindlar, Dr. Marbet, Dr. Montavon. Dr. R. Ruegg, Dr. Schudel, Dr. Schwieter and Dr. Würsch.

Finska Kemistsamfundets verksamhet

Protokoll fört vid årsmötet måndagen den 9 december 1963 kl. 19 i Tekniska Föreningens i Finland lokal. Förhandlingarna leddes av ordföranden, bitr.prof. *Jarl Gripenberg* med undertecknad *Saris* vid protokollet. Närvarande 23 medlemmar.

§ 1. Ordföranden öppnade mötet och hälsade särskilt kvällens föredragshållare från Åbo välkommen.

§ 2. Förrättades val av styrelse för år 1964. Enligt stadgarna kvarstår i styrelsen docent *O. Forsander*, bitr.prof. *J. Gripenberg* samt fil.lic. *N-E. Saris*, den sistnämnde som sekreterare. Till ordförande valdes docent *T-M. Enari*, till viceordförande docent *J. J. Lindberg* och till övriga medlemmar prof. *T. Enkvist*, docent *Ch. Gustafsson*, prof *A. Sundgrén* och tekn. dr. *J. Sundman*.

§ 3. Kassören fil.kand *Karin Sandelin*, arkivarien dipl.ing. *Anna Grönvik* och redaktören docent *T-M. Enari* återvaldes. Till revisorer återvaldes fil.dr. *W. Forsman* och tekn.dr. *G. Silén* med fil.mag. *B. C. Fogelberg* som suppleant.

§ 4. Kassören framförde budgetförslaget för år 1964, som godkändes. Medlemsavgifterna bibehölls oförändrade. Kassörens arvode höjdes till 300 mk.

§ 5. Mötesdagaran för år 1964 fastslogs. Sålunda samlas Samfundet till ordinarie möte den 14 februari samt den andra måndagen i mars, april, oktober, november och december, såvida ej en annan dag befinnes lämpligare.

§ 6. Ordföranden meddelande, att Samfundets styrelse beslutit tilldela prof. emer. *Per Ekwall* bergsrådet Alfthans pris för år 1963 för hans artikel ”Properties and Structure of Systems Containing Association Colloids”, som ingått i Meddelandena No 2, 1963.

§ 7. Fil.mag. *Bengt Skrifvars* höll ett föredrag om ”selektiva jonbytare”. Diskussionsinlägg gjordes av docent *J. J. Lindberg*.

§ 8. Mötet avslutades med samkväm.

J. Gripenberg *Nils-Erik Saris*

Fil.mag. Bengt Skrifvars: Selektiva jonbytare (referat) Har man en utspädd lösning av t.ex. kalciumklorid i kontakt med en katjonbytare i syraform så är vid jämvikt praktiskt taget all kalcium i jonbytarfasen. Denna enkla s.k. „batch„-metod kan tyvärr inte användas alltid. Innehåller lösningen förutom kalcium även andra katjoner i synnerhet om den innehåller andra flervärda joner blir man tvungen att använda kolonn för att få en separering. Möjligheterna blir däremot andra on man använder sig av komplexbildare som överför det ena jonslaget i icke adsorberbar form d.v.s. maskerar det ena jonslaget. Man kan härvid utnyttja komplexstabilitetens surhetsberoende för att få lämpliga betingelser för en separation.

Användingen av kelatbildande maskeriogsmedel ökar möjligheterna för en separation. En besvärlig och tidsödande separation på en lång kolonn kan ofta ersättas med den betydligt snabbare batchmetoden (satsmetoden). Mycket användbart vid separationer vore därför ett harts som i sig själv innehåller kelatbildande grupper. Många dylika hartser har också framställts. Grupper som byggts in i hartser är bl.a. antranilsyra och antranilsyradiättiksyra, fenylendiamin och derivat av denna. Dessa ger koppar- och zinkspecifika hartser. Norrmannen Skogseid lyckades bygga in pikrylamingrupper i hartset och fick härvid en kaliumspecifik jonbytare. Om jonbytaren innehåller endast svagt sura grupper kan man ofta genom variation av surheten få dem selektiva för vissa jonslag.

Att jonbytaren är specifik för en viss jon betyder inte att den ej skulle adsorbera andra joner. Den jonbytande karaktären finns nog kvar d.v.s. jonbytare som innehåller negativa grupper förmår adsorbera alla slag av katjoner om än den föredrar ett visst slag av katjoner.

Det är inte alltid så enkelt att avgöra när en stark adsorption beror av jonparbildning eller kelatbildning och när det är fråga om någon annan effekt.

Detta gäller speciellt joner med hög laddning, vilkas adsorption ur utspädda lösningar alltid är stor.

Ett kelatharts med ett polystyrolhartsskelett är Dowex A-1 Chelating Resin. Detta harts har som aktiv grupp iminodiättiksyra och kan därför väntas starkt adsorbera metaller som bildar stabila komplex med iminodiacetatjonen. Vi har vid Åbo Akademi närmare undersökt detta harts, främst har då undersökts huru distributionskoefficienten för några metaller varierat med yttre lösningens surhet.

Emedan det är fråga om en katjonbytare om än med kelatbildande egenskaper, får man en adsorption av alla katjoner. Däremot kan man vänta sig en betydlig större skillnad i adsorptionen av de olika metalljonerna än vad en vanlig katjonbytare har vid liknande reaktionsbetingelser. Skillnaden i adsorption av natrium och kalcium liksom i adsorptionen av kalcium och koppar bör vara rätt stor.

Jonbytarens aktiva grupp, iminodiättiksyran, är en rätt svag tvåbasisk syra, med konstanterna $pk_1 = 2.65$ och $pk_2 = 9.38$. Detta betyder att jonbytaren inte kan arbeta i starkt sur miljö. Man kan också uttrycka det så att jonbytaren har en stor affinitet till vätejonen och kommer därför att adsorbera denna framom andra katjoner i lösningar med hög vätejonskoncentration.

Beroende på lösningens surhet kommer adsorptionen av metall på jonbytaren att ske på olika sätt. Vi har undersökt upptagningen av en tvåvärd metall ur en lösning av olika surhet och med varierande halt av kaliumjoner. I sur lösning, pH under 2, är adsorptionen oberoende av kaliumjonskoncentrationen men beroende surheten. I alkalisk lösning igen, pH över 12, är adsorptionen oberoende av surheten men beror av kaliumjonskoncentrationen. Vid mellanliggande pH-värden är reaktionen beroende av både lösningens surhet och av kaliumjonskoncentrationen.

Metaller som adsorberas starkt, t.ex. koppar, upptas av jonbytaren även i rätt sur lösning. Denna adsorption är även oberoende av kaliumjonskoncentrationen i lösningen. Däremot är adsorptionen av t.ex. kalcium beroende av kaliumjonskoncentratioen. Kalcium adsorberas inte så starkt av jonbytaren.

Den stora olikheten i adsorptionen av olika metaller gör att jonbytaren är mycket lämplig för separationer enligt satsmetoden eller på en kort kolonn (5—7 cm). Det är dock viktigt att separationsmiljön är den riktiga. Ett för högt pH kan göra att man får adsorption av alla metaller och ingen separation.

En kelatjonbytares selektivitet ligger snarare i adsorptionens surhetsberoende än i en stark adsorption. Det är därför ofta bättre att söka en lämpligare separationsmiljö än att förlänga kolonnen.

Protokoll fört vid Finska Kemistsamfundets möte måndagen den 10 februari 1964 kl 19 i Universitets Kemiska Institut, avdelning Hesperiagatan. Närvarande 29 medlemmar, med undertecknad *Saris* vid protokollet.

§ 1. Till mötets ordförande valdes dipl.ing. *Ragnar Holmström*.

§ 2. Styrelsens årsberättelse för år 1963 upplästes och godkändes.

§ 3. Bokslutet för år 1963 förevisades och godkändes.

§ 4. Revisionsberättelsen upplästes.

§ 5. 1963 års styrelse och kassör beviljades ansvarsfrihet.

§ 6. Minnet av en avliden medlem hedrades med en tyst minut.

§ 7. Centralrådets för Finlands Kemister bokslut och årsberättelse för år 1963 godkändes.

§ 8. Professor *Terje Enkvist* höll föredrag: Kemicum vid Hesperiagatan — Något om nedbrytning av cellulosa-avlutar, om sulfatkoksteori och om Ekmandagarna i träkemi i Stockholm. Diskussionsinlägg gjordes av dr *Lars Andersén*

§ 9. Mötet avslutades med en visning av laboratoriet.

N-E. Saris

Berättelse över Finska Kemistsamfundets verksamhet under år 1963

(Angiven vid mötet den 10 februari 1964)

Samfundet har under året sammanträtt till 6 ordinarie möten, nämligen den 11 februari, 11 mars, 22 april, 22 oktober, 11 november och 9 december. Närvarande har i medeltal varit 28 personer per möte. Den 20 maj anordnade Samfundet en exkursion till Centrallaboratoriums laboratorier i Hagalund.

Vid Samfundets möten har följande föredrag hållits och meddelanden avgivits:

Docent *Ulla Hamberg:* Biologiskt aktiva polypeptider ur blodplasma.

Fil.dr *Veli Kauppinen:* Raudan puutteen vaikutuksesta hiivan kasvuun.

Dr *Rudolf Morf:* International Co-operation in Science, IUPAC in particular.

Dr *Rudolf Morf:* Synthesis and Labeling of Carotene and Carotenoids.

Dipl.ing. *Harald Nyberg:* Ammoniumnitratets sprängtekniska egenskaper.

Fil.lic. *N-E. Saris:* Proteinsyntes — en rapport från Nordiska biokemistmötet i Köpenhamn den 4—5 januari 1963.

Fil.mag. *Bengt Skrifvars:* Om selektiva jonbytare.

Docent *Odd Wager:* Autoimmuna reaktionsmekanismer.

Fil.dr *Örn Wahlroos:* Jonisationsdetektorer i gaskromatografin.

Docent *Henrik Wallgren:* Elektrolytämnesomsättningen i hjärnvävnad *in vitro.*

Under året har fyra nummer av Finska Kemistsamfundets Meddelanden utkommit. Det totala sidoantalet har varit 214.

Vid årsmötet den 9 december tilldelades prof. *Per Ekwall* bergsrådet Alfthans pris för år 1963 för uppsatsen "Properties and Structure of Systems Containing Association Colloids", som ingått i Meddelandena No 2, 1963.

Till styrelsens kännedom har kommit, att en av Samfundets medlemmar avlidit, nämligen:

fil.mag. *Gösta Hortling.*

Tolv medlemmar har avgått. Samfundet har invalt 17 nya medlemmar. Medlemsantalet är 390. Styrelsen har sammanträtt sex gånger. Dess sammansättning har varit följande:

ordförande: bitr.prof. *Jarl Gripenberg*
viceordförande: docent *T-M. Enari*
sekreterare: fil.lic. *Nils-Erik Saris*
medlemmar: prof. *Terje Enkvist*
docent *Olof Forsander*
docent *Charley Gustafsson*
docent *J. Johan Lindberg*
prof. *Albert Sundgrén*
tekn.dr *Jacobus Sundman*

Samfundets funktionärer har varit:

kassör: fil.kand. *Karin Sandelin*
arkivarie: dipl.ing. *Anna Grönvik*
redaktör: docent *Tor-Magnus Enari*

Revisorer har varit: fil.dr. *William Forsman* och tekn. *Gösta Silén* med fil.-mag. *B. C. Fogelberg* som suppleant.

Samfundets representanter i Centralrådet för Finlands Kemister har varit prof. *Terje Enkvist* och bitr. prof. *Jarl Gripenberg.*

Samfundet har tillsammans med Suomalaisten Kemistien Seura tillsatt en kommitté för handläggandet av Föreningens Acta Chemica Scandinavica ekonomi. Samfundets representant i kommittén har varit kassören, fil.kand. *Karin Sandelin.*

J. Gripenberg
ordförande

N-E. Saris
sekreterare

Helsingfors 1964, Frenckellska Tryckeri Aktiebolaget