Abstracts of PhD conference 2006

László, Krisztina (ed.) (ed.)

Formation and Detection of Clay Network Structure in Poly(propylene)/Layered Silicate Nanocomposites

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Polypropylene (PP) has received increasing attention over the last decades due to the extension of its property envelope. Recently, many attempts are in progress to modify PP with layered silicates to prepare nanocomposites. The exfoliation of the clay usually does not take place spontaneously during processing [1]. In order to help exfoliation or the formation of an intercalated structure, functionalized polymer, maleinated PP (MAPP) is added to the composite.

Some layered silicates easily exfoliate in water to individual silicate layers. Face to face interactions of these layers lead to aggregation, while edge to face interactions result in the formation of a network, the so-called house-of-cards or skeleton structure. Both interactions are claimed to occur also in PP/layered silicate composites. Relatively little is known about the formation of the network structure and its effect, although some sources claim that it should improve composite properties [2].

The detection of house-of-cards structure is not always unambiguous. Usually, the network is detected either by transmission electron microscopy (TEM) or rheology, or both. The existence of the network could not be proved unambiguously with the usual techniques, *i.e.* with TEM or by plotting viscoelastic properties as a function of frequency. TEM can only analyse a very small area and two dimensional micrographs can prove the existence of a three-dimensional network structure. The formation of the network substantially modifies the rheological properties of nanocomposite melts. Cole-Cole plots detect the formation of the network very sensitively Fig. 1 [3]. A certain number of
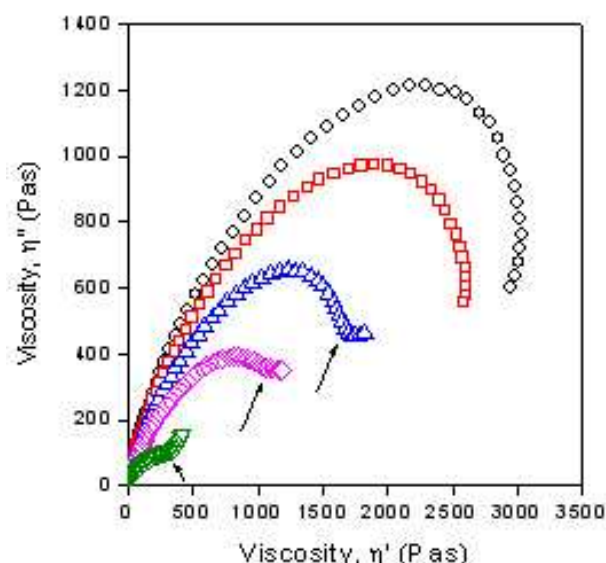

Fig. 1. Cole-Cole representation of the viscoelastic properties of PP/OMMT/ (MAPP) nanocomposites

silicate layers are needed to create a house-of-cards structure. A threshold concentration of MAPP exists in the investigated system, which depends on silicate content. The degree of exfoliation can also be detected from rheological parameters, like yield stress or shear thinning exponent [4].

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Thermoplastic Starch/Layered Silicate Composites: Structure, Interaction, Properties

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Recently, the increasing amount of polymer waste is one of the most challenging problems the world faces, due to the large volume and the slow degradation of the polymeric products. The application of biodegradable polymers, which are primarily natural polymers such as starch and cellulose, can be an alternative solution, since these materials are easily available at low cost, renewable, and fully degradable. Widespread use of biodegradable materials is limited by their processability, *e.g.* the melting point of starch (T_m = 257 °C) is higher than its degradation temperature (T_d = 230–250 °C). However, by the application of plasticizers the starch can be transformed into a thermoplastic material.

In the experiments, using two different mixing procedures, we succeeded to produce composite materials with various mechanical properties and plasticizer contents. The samples were prepared with 30 to 50 wt% glycerol content, followed by structure and mechanical tests on them. Dried starch and dried glycerol plasticizer were used in the experiments since the presence of absorbed water hinders the polymer processing procedure. The obtained products exhibited good mechanical properties, but have failed with longer storage time due to the high water uptake as a consequence of the strong hydrophilicity of the starch.

In order to further improve the mechanical properties and the life-time of the products different composites were prepared and processed. First, thermoplastic starch (TPS) nanocomposites were prepared by using differently surface treated layered silicates, then structure-property studies were performed on these samples [1].

It is necessary to improve the processability of TPS composites as well as to decrease the shrinkage of the injection of moulded products. The development of fiber reinforced thermoplastic starch systems having improved mechanical properties and lower shrinkage is planned.

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Aptamer Selection for Macromolecular (Protein) and for Small Molecule Targets

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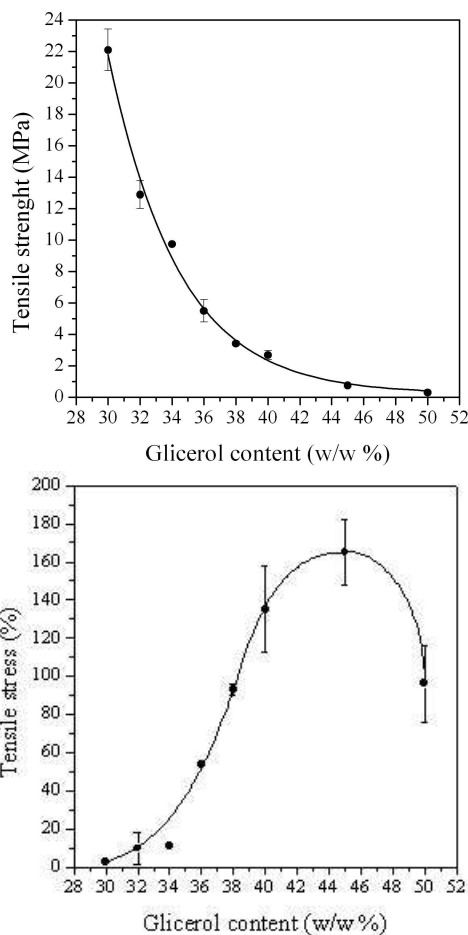Supervisor: Tamás Mészáros
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Fig. 2. Mechanical Properties of Glycerol Plasticized Thermoplastic Starch

Aptamers are 20-80 nucleotide long RNA or single stranded DNA molecules which bind to panel of targets – ranging from protein to small organic molecules – with high affinity and specificity [2].

In our experiments we produced aptamer candidates for the GST-tagged MPK4 protein and for a mycotoxin, called Ochratoxin-A, both immobilized on Sepharose resin. The aptamer selection was performed by SELEX (systematic evolution of ligands by exponential enrichment) procedure (Ellington 1990, Tuerk 1990). In the initial round of selection a single stranded random sequence DNA library was incubated with the target and the specifically bound sequences were amplified by PCR reaction. In the following rounds of selection single stranded DNA sequences from the previous cycle were used as a starting library. In both cases 15 rounds of selection and 4 rounds of contraselection were made. After the final round of selection the double stranded DNA from the terminal PCR reaction was ligated and cloned into p-Gem-T-Easy vector. The vector constructs were transformed into *Escherichia coli* DH5α strain. The bacterial colonies were checked by PCR with p-Gem-T-Easy specific primers. Individual colonies containing the possible aptamer candidates were sequenced. In both cases we found sequences with high similarity, and some sequences were isolated more than once implying high affinity for the given

target. The MPK4 aptamers contained T and G rich sequences and common structural motifs.

Functionality of putative MPK4 aptamers will be tested with Western-blot, and affinity purification of the target. Binding capacity of aptamer candidates of Ochratoxin-A will be studied by competitive inhibition of ELISA detection of the toxin.

In the present lecture main steps of the SELEX experiments for the selection of MPK4 and Ochratoxin-A aptamers will be detailed. Potential aptamer candidates for the selected targets will also be presented.

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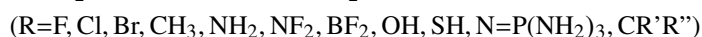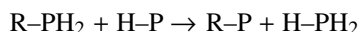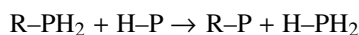### Could stable phosphinidenes be synthesised?

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Phosphinidenes (R–P) have been observed in many reactions as unstable and reactive intermediates but they have never been synthetised as stable compounds [1]. A new synthetic concept is the didehalogenation of R–PCl$_2$ compounds. The relative stability of different phosphinidenes has been investigated using the isodesmic reaction:

$$R–PH_2 + H–P \rightarrow R–P + H–PH_2$$
$$R–PH_2 + H–P \rightarrow R–P + H–PH_2$$
$$(R=F, Cl, Br, CH_3, NH_2, NF_2, BF_2, OH, SH, N=P(NH_2)_3, CR'R'')$$

The energies of these reactions with different R groups have been calculated with DFT- and Møller-Plessett methods at different levels of theory (B3LYP/3-21G*, B3LYP/6-311+G**, MP2/6-31G*). If the energy of this isodesmic reaction is positive, the R-P phosphinidene is less stable than the H-P. The best stabilizing groups are those where an N or S atom is attached to the phosphinidene. The R'$_2$C=N- group turned out to be especially effective. Further optimization is possible by varying the R' substituents of the R'$_2$C=N moiety, *i.e.* by varying the polarity of the C=N bond. If the carbon is a member of a ring (triafulvene (**1**) and pentafulvene (**2**) compounds), the stabilizing effects are different:
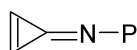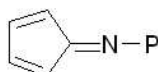
(**1**)   (**2**)

The best stabilizing effect is provided by the pentafulvene-compound (**2**) (cca. 60 kcal/mol at various levels of theory).

In further studies the singlet-triplet splitting has been investigated. Most of the phosphinidenes above have triplet ground state. Exceptions are those with substitutes: H$_2$N–P, F$_2$N–P, H$_2$C=N–P, and the fulvene compounds. These turned out to be the most stable compounds in the isodesmic reactions. A relatively good correlation has been observed between the singlet-triplet energy-differences and the reaction energies of the isodesmic reaction (R^2 is more than 0,9 at different levels of theory for 15 compounds).

The most important factor of the stabilities of transient compounds is their resistance against dimerisation, thus the reactivity of (**2**) in different dimerization reactions will also be discussed.

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The rate of crystal growth as a factor contributing to attain successful optical resolution in the case of the optical resolution of *N*-formylphenylalanine by α-phenylethylamine

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Production of optically pure compounds is usually based on chiral recognition processes in solution during the formation of solid (crystalline) phase. The interactions of the enantiomers and the resolving agent in the saturated solution can be described on the basis of thermodynamic equilibria using phase diagrams. The thermodynamic approach usually gives the correct description of the processes [1, 2]. In some cases, kinetic factors can have determining role in the processes and thus affect the attainable efficiency of the optical resolution [3]. Kinetic processes can even result in enhanced resolution efficiency.

The optical resolution of phenylalanine through its *N*-formyl derivative by α-phenylethylamine resolving agent *via* diastereomeric salt formation is an effective procedure known from literature [4].

rac-N-formylphenylalanine   *(S)-(-)-α*-phenylethylamine   pure *(S)-(+)*-N-formylphenylalanine
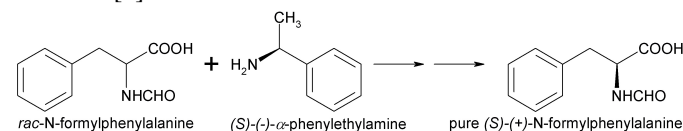
The above process has high efficiency although the diastereomers have similar thermodynamic stabilities. It is the difference in the rate of crystal growth that makes possible to attain high optical purity and yield during the process. As illustrated by the photographs below the crystal growth of the more soluble diastereomer is strongly inhibited in two directions.
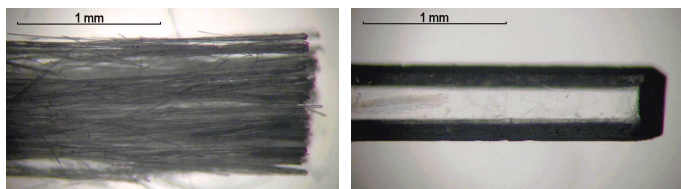
Fig. 3. *(a)* Inhibited crystal growth in perpendicular directions to the longitudinal axis *(b)* No crystal growth inhibition

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A Comparative Study of Waste Solvent Treatment Processes

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The great extent of solvent utilization in the chemical industry generates a charge of the waste solvent treatment solution possibilities. The aim of this study is a comparison of two waste solvent mixture treatment processes, distillation and incineration from ecological point of view. To evaluate these methods the several emissions need to be comparable, therefore the Life Cycle Assessment method is appropriate. The waste solvent mixture, containing mainly acetone, produced at Richter Gedeon Rt. gives the basis of the evaluation.

Due to the given informations by the solvent recovery unit of Richter Gedeon Rt. and Onyx Kft. it was possible to acquire the technologies of both methods, what enables us to define the system boundaries, modules and the inputs and outputs in both cases. According to the material and energy balances of the several moduls in the next part of the work we made the enviromental load calculations by use of the SimaPro 6 software. For these calculations we choosed the Eco-Indicator 99 method, which defines 11 categories.

The calculated results and the comparison of the waste solvent mixture treatment methods are shown in the diagram:

As the diagram shows, 4 environmental categories are significant from the comparative point of view, such as Ecotoxicity, Fossil fuels, Global change and the Respiratory effects caused by inorganic substances.

According to the results it is clear, that the incineration of the waste solvents causes less environmental load on the basis of the examined conditions. However for the exact conclusion are neccesarily needed the evaluations of the related processes,
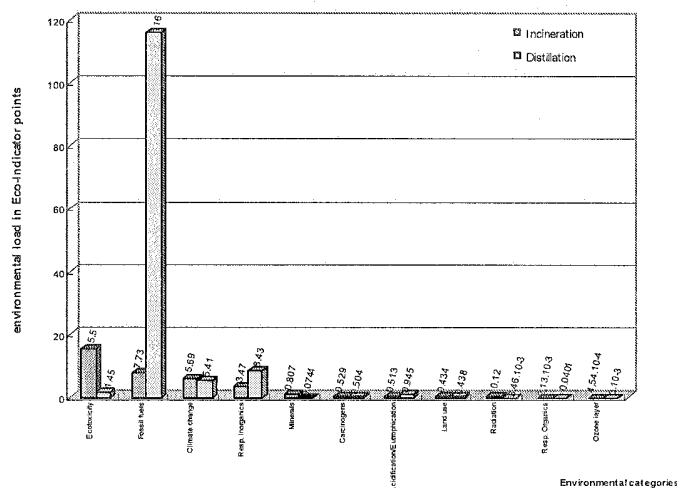

Fig. 4.

especially the acetone production, which effects higher environmental damage in the case of incineration method.

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Characterization of tailor-made Rh-Sn/Al2O3 catalysts by Mössbauer spectroscopy and methylcyclopentane ring opening reaction

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Sn was added to a 1% Rh/Al_2O_3 catalyst (D=75%) by controlled surface reaction (CSR) [1, 2] of $Sn(n-C_4H_9)_4$ in amounts corresponding nominally to 1/4, 1/2, 1 and 2 monolayers. The Sn-Rh catalysts were characterized by hydrogen chemisorption, TEM, CO-FTIR, Mössbauer spectroscopy [3] and in test reaction of methylcyclopentane (MCP) [4]. Three different Sn phases were found after reduction (Table): SnO_2, Sn-rich and Sn-poor RhSn alloy [5]. Tin transformed entirely to SnO_2 upon oxidation. The effect of oxidation (373 K) and reduction (at 473 K) appeared to be reversible. The 1 monolayer Sn-Rh sample behaved in MCP transformation similarly to a catalyst with small Rh ensembles while the product pattern of other Sn-Rh catalysts was similar to that produced by larger Rh ensembles (Table). The suggested model is as follows: Sn was deposited selectively on low-Miller-index microfacets of Rh when its introduced amount was lower than 1 monolayer. Increasing the introduced amount of Sn led to its deposition also on high-Miller-index sites (random deposition).

		^{119}Sn-Mössbauer: distribution of Sn phases after 2nd reduction			MCP Ring opening reaction, p(MCP), p(H$_2$)=13:160 kPa, T=483 K				
		SnO$_2$	RhSn$_x$ phase		TOF,	Selectivity, %			
Samples	D %		x ≈ 4	1<x<2	h^{-1}	<C$_6$	2MP	3MP	nH
Sn2	15	24	35	40	0	-	-	-	-
Sn1	21	27	33	40	17	25	34	16	25
Sn1/2	35	22	31	47	33	34	32	17	17
Sn1/4	51	21	20	59	23	41	26	13	20

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The Extraction of *Vitex agnus castus* with Different Solvents

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Recently, more attention has been paid to healthy way of life, mainly to the importance of healthy nutrition intake. First of all it means fibre-full and cholesterol-less nutrition intake, as well as solvent residual-free natural products are favoured. The supercritical fluid extraction (SFE) is one of the separation processes that produces solvent residual-free products, allows the extraction of heat-sensitive compounds, and is an environmentally accepted technology.

The goal of this work was to extract valuable components and natural agents from the fruit of chaste tree (*Vitex agnus castus* L.). Laboratory and pilot plant extractions were carried out using different solvents.

For the laboratory Soxhlet extraction of *Vitex agnus castus* seeds four different solvents (*n*-hexane, ethyl-acetate, isopropyl-alcohol, ethyl-alcohol) were applied, all of them are permitted extraction solvents. Increasing the polarity of solvents higher extraction yields were achieved (*n*-hexane: 6.37 %; ethyl-acetate: 10.12 %; isopropyl-alcohol: 13.46 %; ethyl-alcohol: 18.11 %).

Pilot plant experiments were performed in a Soxhlet extractor with ethyl-alcohol (96 % of purity), and in a 5 L volume high-pressure vessel with supercritical CO$_2$ using various pressure and temperature conditions. The pressure was changed from 100 bar up to 450 bar and the temperature was adjusted between 40-60 ˚C. In a sample case 5 % ethyl-alcohol was added to the sc-CO$_2$ as entrainer (at 300 bar and 40 ˚C). The yields changed within a wide range (0.19 % - 9.97 %) according to the solution power of the supercritical fluid.

The extract samples were analysed by NMR, MS, and HPLC methods. Some compounds were isolated from the *Agni casti fructus* for the first time like vitetrifolin B, vitetrifolin C and eupatorin. Furthermore, rotundifuran, vitexlactone, spathulenol,
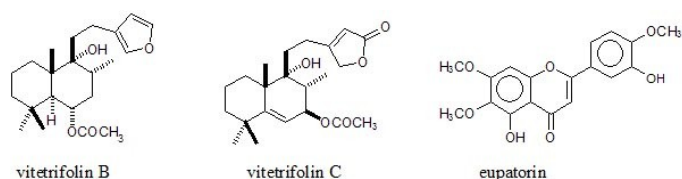

vitetrifolin B   vitetrifolin C   eupatorin

Fig. 5.

and two flavonoid derivatives were identified by NMR technique. The flavonoid derivatives were casticin and penduletin. Chaste tree extracts were examined with *in vitro* antioxidant assay. This was an enzyme-dependent system of lipid peroxidation.

The chaste tree extract is capable for treatment of premenstrual syndrome (PMS). A product was developed by Gradiens Ltd. which contains *Vitex agnus castus* extract as main constituent. A HPLC method was validated providing a possibility to the qualitative and quantitative determination of casticin from extracts or products originated from chaste tree.

Experimental Data Based Modelling and Simulation of Isopropanol Dehydration by Pervaporation

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Pervaporation is a widely used membrane technique for the separation of liquid mixtures [1]. Pervaporation is most suitable for the separation of close boiling or azeotropic mixtures. One of the most frequent industrial application areas of pervaporation is the dehydration of solvents that form an azeotrope with water [2], like e.g. ethanol, isopropanol, tetrahydro-furane etc.

Due to its high selectivity and low operational costs [3], pervaporation can be a useful alternative to distillation. As the attainable pervaporation fluxes are relatively low, large membrane surfaces are to be applied when large amount of feed is to be processed. The combination of distillation and pervaporation may result in cost effective hybrid systems that can process a large amount of feed mixture [1,4,5].

The design and optimization of process flow sheets can be facilitated using commercially available flow sheet simulation software. The permeation properties of the pervaporation membranes depend on the membrane type, therefore, any modelling procedure should be based on experimental data.

At first, isotherm experiments were carried out at three different temperatures (60, 80, 90°C) using a hydrophilic flat membrane sheet (PERVAP 2210, Sulzer Chemtech). The permeate fluxes, as well as the feed and permeate compositions were measured. A solution-diffusion model was used for modelling the membrane transport. The model parameters were fitted to the experimental data. An earlier developed, user-added pervaporation module within the ChemCad flow sheet software package was applied with success. After formulating the mass and heat balance equations of the user-added pervaporation module, the fitted transport model parameters were used for the simulation of our measured data. Finally the simulation of an industrial scale pervaporation apparatus and a hybrid system was carried out. Simulated and measured industrial data were compared. Our model describes the experimental data quite well.

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Smart nanocomposite polymer membranes with on/off switching control

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Stimuli-responsive membranes have attracted widespread interest in the past decade. For these membranes the period and rate of transfer can be controlled by external or environmental influence (e.g. temperature, pH, electric or magnetic field etc.) [1].

The aim of my PhD work was to prepare stimuli-responsive composite-gel membranes containing ordered micro channels.

These membranes can act as "on-off switches" or "permeability valves". The duration and the rate of the mass transfer can be controlled by external triggers like temperature or magnetic field. The channels are designed to contain an ordered array of stimuli responsive core-shell type gel beads that can change their size according to the external stimuli. The composite-heterogeneous gel membrane consisting of core-shell magnetic latex particles [magnetic polystyrene/poly(N-isopropylacrylamide) (MPS-PNIPAAm)] dispersed within a PVA network was developed as a temperature - responsive membrane [2]. The core–shell magnetic latex particles containing poly(N-isopropylacrylamide) in the shell were prepared by encapsulation of magnetic polystyrene core using a precipitation polymerization process.

A new thermoresponsive composite-gel membrane capable of regulating permeability in response to external temperature change has been demonstrated by a permeation study of bovine serum albumine, [BSA], methylene blue [MB], and riboflavine [RF]. An Agilent 8453 UV-Visible spectro-photometer was used to measure the absorbancy as a function of time at a wavelength of 278 nm. In order to relate the absorbancy to the concentration of the permeant, calibration measurements were performed. The result indicates reversible change in the permeability of the membrane that was controlled by the temperature.

Potential application of specially designed micro channel structures cover a broad spectrum of application, such as micro filtration, flow control, molecular separation, biomolecule purification, fractionation and controlled drug delivery.

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Synthesis of Heparanase Inhibitors, Heparin Disaccharides Possessing an Azasugar Unit

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Tumor metastasis occurs via complex multistage processes, which involve tumor cell adhesion to various basement membrane components and degradation of the extracellular matrix and basement membranes. Glycosaminoglycans, such as heparin and heparan sulphate, are important constituents in these structures. Cleavage of heparan sulphate by the endoglucuronidase enzyme heparanase, plays a crucial role in a number of biological processes, including the cell invasion of some malignant solid tumors through basement membranes [1]. The pos-

sibility of antimetastatic cancer therapies based on the inhibition of heparanase is intensely investigated.

Azasugars are well-known inhibitors of various glycosidases. As monosaccharide azasugars inhibit several glycosidases, to incorporate specificity for heparanase inhibition we have designed pseudooligosaccharides mimicking structural motifs of heparin and heparan sulfate.

We now report the preparation of three different disaccharides (**4,5,6**) possessing an aza-L-idopyranose unit [2]. The 1,5-dideoxy-1,5-imino-L-iditol derivative (**2**) was glycosylated with the thioglycoside donor (**1**) to afford the protected pseudodisaccharide derivative (**3**) stereoselectively.
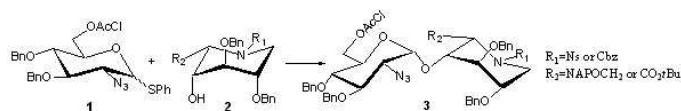
Deprotection, N-acetylation and O-sulfation of **3** afforded the free heparanase inhibitors (**4,5,6**).
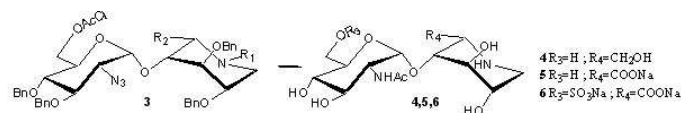
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Wood Flour Filled PP Composites: Adhesion, Deformation, Failure

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The interest in using raw materials from renewable resources increased considerably in recent years. Wood flour and other natural polymers have numerous advantages: availability, excellent mechanical properties and acceptable price [1]. Naturally, these materials also have some drawbacks: properties depend on origin, they change from year to year, the fibers are sensitive to moisture and their transverse strength is small. Adhesion and processability must be optimized if we want to prepare wood flour filled plastics with high filler content. Because of the large size of the filler and its low surface free energy only weak interaction develops between the components. This leads to easy debonding and premature failure of the composites under the effect of external load.

The goal of this study was to obtain information about the tensile, impact and failure characteristics of wood flour filled PP composites. Micromechanical deformations were investigated with acoustic emission and volume strain measurements and an attempt was made to identify the main process causing the failure of the composites. The structure of the composites was studied by SEM on fracture surfaces. The adhesion of the components was improved by the application of maleinated polypropylene (MAPP).
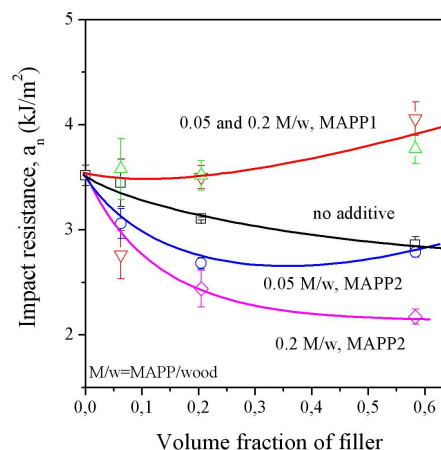
Fig. 6. Effect of the type and amount of maleinated PP on the notched charpy impact strength of PP/wood composites

The study of the mechanical properties of PP/wood composites showed that stiffness increases with wood content and it does not depend very much either on the type or the amount of the functionalized polymer used. On the other hand, ultimate tensile properties are strongly influenced by the amount and properties of MAPP; larger molecular weight and smaller functionality are more advantageous both for strength and impact resistance (Fig. 6). Due to their large size, wood particles debond very easily from the matrix leading to volume increase and catastrophic failure at small deformations. When adhesion is improved by the introduction of MAPP, large wood particles fracture thus also contribute to the failure of the composite. At large wood content considerable aggregation of the particles may take place leading to inferior strength [2].

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A new regio- and chemoselective reductive cleavage of cyclic acetals

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The regioselective reductive ring opening of cyclic benzylidene acetals to *O*-benzyl ethers is a frequently used reaction for the preparation of partially protected carbohydrate derivatives. Various methods have been introduced for the reductive cleavage of 4,6-*O*-benzylidene hexopyranosides to the corresponding 4-*O*-benzyl ethers including $LiAlH_4$-$AlCl_3$, BH_3Me_3N-$AlCl_3$, BH_3Me_2NH-BF_3Et_2O and BH_3THF-Bu_2BOTf as reagents[1]. These methods suffer from various drawbacks, such as incompatibility with common protecting groups, unsatisfactory regioselectivity, moderate yields of the desired products and variable regioselectivity depending on the substrate and on the solvent.

We have studied the reductive ring opening of 4,6-*O*-benzylidene hexopyranosides using various combinations of Lewis acids and hydride donors and developed a highly regio- and chemoselective ring opening reaction which provides 4-*O*-ethers from cyclic 4,6-*O*-benzylidene type acetals in consistently high yields.

The regioselectivity of the ring opening of a 4,6-*O*-benzylidene-glucopyranoside was investigated using combinations of borane complexes (BH_3Me_3N, BH_3Me_2S, BH_3THF) with Lewis acids. It was found that BH_3THF provided the 4-*O*-benzyl ethers with highest regioselectivity. The effect of Lewis acids was studied by testing a series of common Lewis acids ($TMSOTf$, $Sc(OTf)_3$, ZnI_2, $AlCl_3$, BF_3Et_2O) in combination with BH_3THF. The regioselectivity of the ring opening was not affected, in all cases the 4-*O*-benzyl ether was obtained almost exclusively. On the other hand, the reaction rate was strongly influenced by the choice of the Lewis acid.

From the reagents studied $BH_3.THF$-$TMSOTf$ was selected for further investigations, and a series of carbohydrate 4,6-*O*-benzylidene acetals was reduced in CH_2Cl_2. In all cases, the reactions gave the 4-O-benzyl ethers in high yields.

Ph / O—O / R_2O / OR / OR$_1$ | $BH_3.THF$ / $TMSOTf$ / 90-100% → | OH / BnO / O / R_2O / OR / OR$_1$
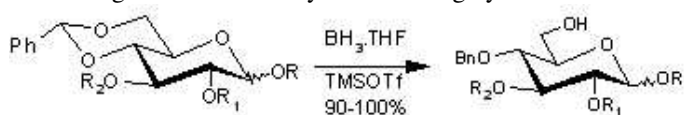
The regioselectivity and the yields were unaffected by the steric bulk of the 3-*O*-substituents, the type of ring annelation and, in contrast with other ring opening methods, the same regioselectivity was observed by changing the solvent to THF. The reaction is compatible with the most common protecting groups, including benzyl, *tert*-butyldimethylsilyl, acyl, benzyloxycarbonyl and fluorenylmethoxycarbonyl groups. Furthermore the reaction could also be performed in the presence of free hydroxyl as well as azido and thioglycoside functions. The reaction was extended to the reductive cleavage of *p*-methoxybenzylidene and 1-naphthylmethylidene acetals, affording essentially the same results. In case of 1,3-dioxolane type benzylidene acetals, the regioselectivity was determined by the configuration of the acetal carbon.

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Investigation of Nanoparticulate thin Films by Scanning Angle Reflectometry and UV-Vis Optical Spectroscopy

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Nanostructured thin layers attracted significant attention during the last two-decades due to their potential applications in optical, electro-optical and magnetic devices. In this study we present a novel application of scanning angle reflectometry (SAR), for the characterization of particulate nanostructured films prepared on solid supports. The main advantage of SAR, in contrary to the spectral methods, is that the dispersion of refractive index does not need to be taken into consideration, and is especially sensitive to the optical properties of ultra thin (macro)molecular films. This measurement technique can provide information about some characteristic parameters of thin films (*e.g.* thickness and effective refractive index) and is used mainly for monitoring polymer adsorption processes at the solid/liquid interface near the Brewster angle of the substrate [1]. The main purpose of this work is to verify the applicability of SAR to solid supported particulate films and to determine the aforementioned parameters.
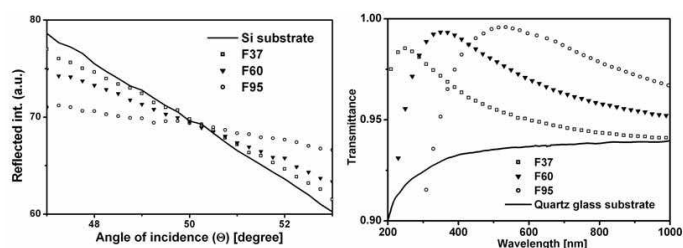

Fig. 7. Reflected intensity as a function of the angle of incidence and transmittance as a function of the wavelength for the investigated monoparticulate LB films prepared from different sized particles. The numbers in the legend refer to the appropriate particle diameters in nanometer.

We prepared three different silica nanoparticle samples by a sol-gel route, applying Stöber's method [2]. The mean particle sizes were determined by transmission electron microscopy (TEM). Nanostructured Langmuir-Blodgett (LB) films of the Stöber-silica nanoparticles have been prepared on both silicon and quartz glass substrates. The deposited films were investigated using scanning angle reflectometry and UV-Vis spectroscopy. The reflectivity and the transmittance spectra of the LB films were evaluated using optical models based on thin layer optics [3, 4]. Film thickness and effective refractive index of the films were determined. From the refractive index values the volume fraction of the particles in the film was estimated by the Lorentz-Lorenz effective medium approach.

We demonstrate that SAR can be applied for the investigation of the prepared nanostructured films on solid supports. Moreover, there is a fairly good agreement between the results of the

applied optical methods, which proves the validity of the theoretical model used to evaluate the measurement data.

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Thermal Characterization of Hair Using TG-MS Combined Thermoanalytical Technique

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Our aim was to investigate four amino acids (aspartic acid, glutamic acid, histidine and tyrosine, analytical grade) and four hair samples in order to get information on their thermal decomposition using combined (TG-MS) and DSC techniques.
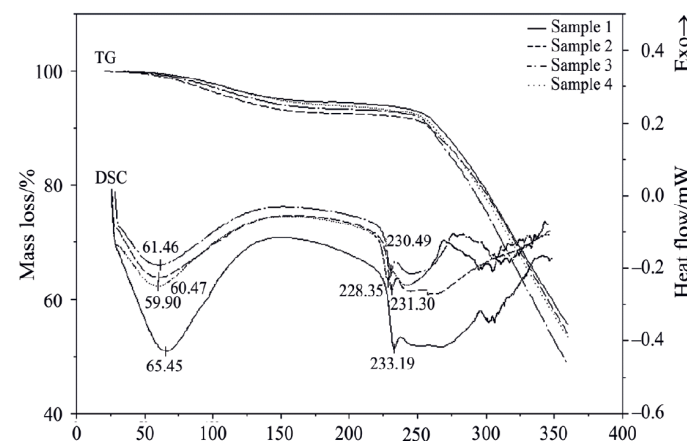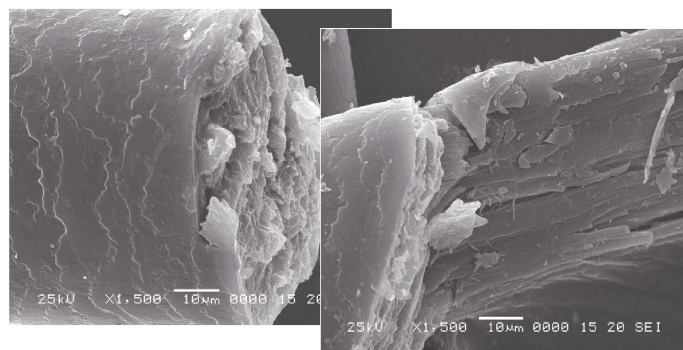
The hair samples were collected from the posterior vertex region of scalp and cut as close as possible to the skin. All samples were stored at room temperature.
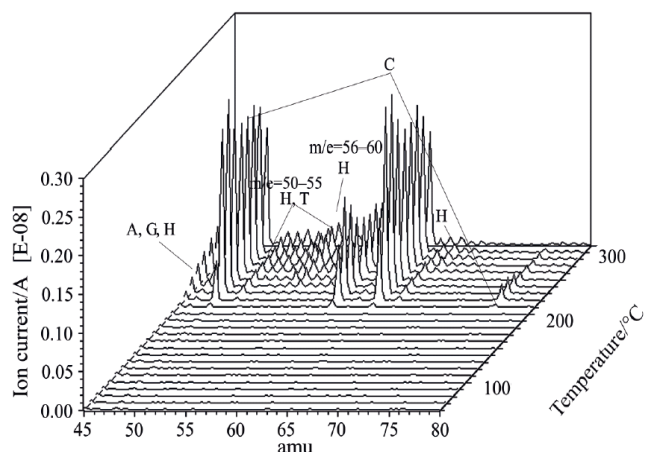
Hair sample 1, β=50°C min^{-1}, interpretation of specific mass units;
(A – aspartic acid, G – glutamic acid, H – histidine, T – tyrosine)

The evaluation of DSC and TG curves of amino acids shows that all substances possess an endothermic decomposition accompanied by different mass losses. Among the investigated amino acids histidine showed the least and tyrosine the highest thermal stability.

Interpreting the mass spectra of these samples, since they contain identical functional groups (-NH$_2$, -COOH), some common fragmentation features were observed. However, due to their different chemical composition remarkable differences have also been recognized.

The thermoanalytical curves of different hair samples showed no substantial differences. Minor deviations were found in their moisture content and temperatures of endothermic peaks belonging to the melting of α-keratin.

Comparing the mass spectra of α-keratin and the hair samples the most characteristic signals appeared at the same m/e values. The evaluation of the mass spectra of the pure amino acid samples helped us to identify their fragmentation from the hair matrix.

We have also investigated the influence of the different heating rates on the thermal decomposition of hair samples. The application of the higher heating rates led to the following observations in the mass spectra:

- two orders of magnitude higher ion currents were recorded,

- relative intensities of some peaks have changed,

- alteration have been found in the curvature of the MID lines.

The origin of the hair samples did not affect remarkably their decomposition character. However, these results can provide possible starting points in the analysis/identification of the infiltrated medicines and their metabolites in the hair. To obtain reliable results, the geographic and ethnic origin, moreover the

effect of different treatments (e.g. dying, perming) should be taken into account.

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Study of the Coagulation of a Styrene-butadiene Copolymer

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Synthetic rubber is used in many fields as raw material. The car industry, especially the tire manufacturing is one of the greatest consumers, since the cap of the tire is mostly made from ESBR. Other ESBR polymers are used in some other car parts. This type of rubber is part of our everyday life in such an exotic form as a chewing gum.

Styrene-butadiene copolymer is manufactured in the chemical industry in two different continuous technologies, i.e. solution and emulsion polymerization. Both technologies include a finishing step to separate the latex from the reaction solution. In case of emulsion polymerization it is the coagulation of latex particles. Coagulation is achieved in two different ways. The first technology is based on the sequential addition of various chemicals in a cascade system to break the colloidal equilibrium, the second on strong mechanical stress. From May till
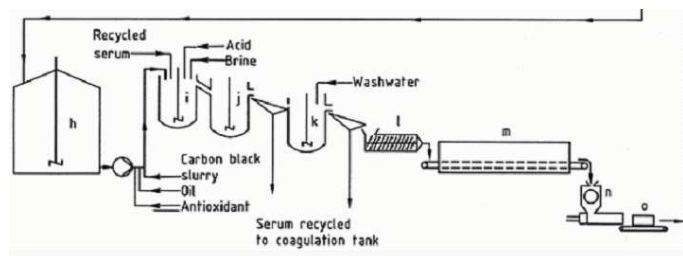

Fig. 8. Cascade for latex finishing i. Coagulation tank; j. Soap conversion tank; k. Wash tank; l. Dewater extrudes; m. Dryer; n. . . . o. Packaging

October, 2005 the author worked on the optimization and intensification of such a coagulation technology at Dow Chemical Company, Schkopau, Germany. The main problems of technology were caused by the fact that the chemistry of the process has

never been properly investigated or documented, the production was carried out on the basis of "good practise" and empirical knowledge of workers, but this was not enough to answer new challenges and problems. A literature review of the colloidal stability of polymer emulsions has been compiled. Batch and semi-batch laboratory experiments have been carried out to determine the effect of various added chemicals. Technological modifications were recommended by the author and subsequently applied in the plant to result a successful production intensification in the last months.

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Synthesis of Optically Active Oxirane and Dihydropyrrole Derivatives

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In the framework of scientific cooperation between our research group and the CNR Institute in Florence optically active oxirane and oxetane derivatives have been synthetized [1, 2]. Earlier I dealt with the preparation of optically active aminooxirane derivatives by separation of their diastereoisomeric salts [3].
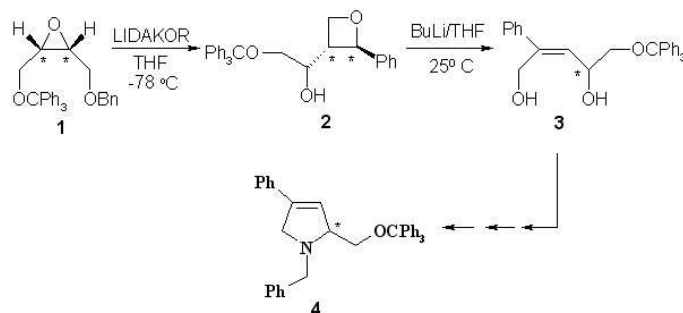
Recently our research group has developed a new enzyme catalysed method for separation of the enantiomers of (*Z*)-2-trityloxymethyl-3-hydroxymethyl-oxirane. In my work this kinetic resolution was optimized applying a new enzyme. Thereafter the formed optically active oxirane was transformed into compound **1**. Oxirane **1** was transformed into oxetane (**2**) and diol (**3**) using base promoted enantioselective rearrangement reactions (developed by our group). The diol **4** yielded the new 1-benzyl-4-phenyl-2-trityloxymethyl-2,5-dihydropyrrole (**4**) via mesylation and consecutive ring closuring reaction with benzylamine. We carried out these reactions starting from both the racemic and the optically active diol (**3**). Starting from optically active diol (**3**) we got optically active dihydropyrrole derivative

(**4**), consequently the ring closuring reaction is enantioselective. The derivatives of the synthetized compound can be valuable intermediates of drugs in pharmaceutical research, and can be used as chiral ligands in enantioselective catalytic reactions.

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Developing Light Protecting Molecules

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In our days the importance of the light-stability agents is increasing because of the ozone layer getting more and more thinner. Most of them protect only against the UVB light, but they slightly protect against the UVA, which is the most dangerous component of the sunlight.

Combination of Mexoryl XS and Mexoryl XL molecules – which were developed in the L'Oreal's laboratory – with other agents (for example titanium-oxide) yields excellent light-stability agent.

The derivatives of Mexoryl have good properties; they are stable, resist to the sunlight, non-irritating and non-allergenic.

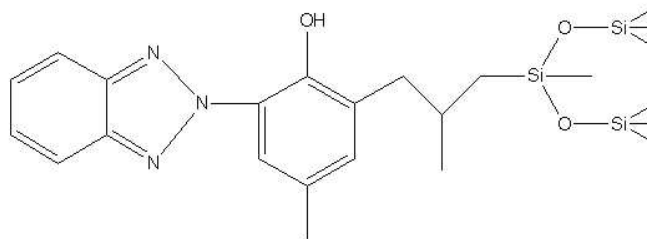I am working on the synthesis of Meroryl XL and its analogs:

Fig. 9. Mexoryl XL

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Optimization of Multicommodity Transportation and Supply Chain Problem

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The transportation problem of a commodity, as originally defined by Appa [1], deals with a set of source sites and a set of destinations. The task is to satisfy all the demands of destinations and utilize all the supplies of source sites with minimum transportation cost. This is the basis of much more complicated problem classes. According to Vidal and Goetschalckx [2], for example, the problem of supply chain allocation and distribution involves the determination of the number, location, capacity, and type of manufacturing plants and warehouses to use; the set of suppliers to select; the transportation channels to use; the amount of raw materials and products to produce and ship among suppliers, plants, warehouses, and customers; and the amount of raw materials, intermediate products, and finished goods to hold at various locations in inventory.

I deal with the problem class, where not only the transportation volumes are to be optimally assigned but the opening or closing of some manufacturing plants is also to be decided together with their production volume, in order to satisfy, with minimum cost, a set of demands on several product kinds at several locations, and where the fix cost of plants can be expressed as a stepwise constant function.
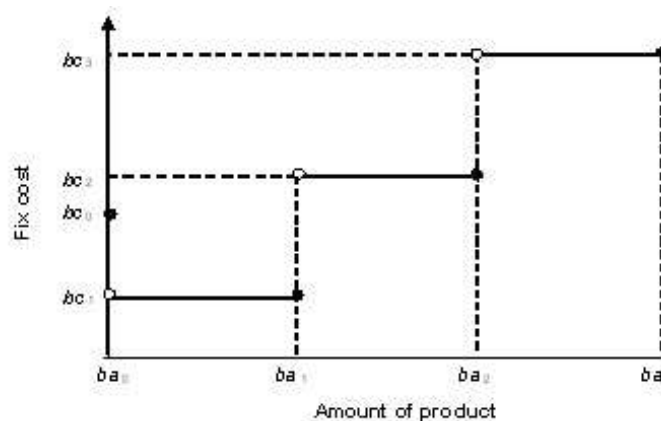
Fig. 10. Stepwise constant cost function

Tab. 2. Comparison on a small scale problem

Model	Iterations	CPU (sec)
Multi-M	3384	1.046
Convex Hull	1121	0.453
Türkay and Grossmann	2350	0.750
New model	543	0.312

The stepwise cost function is a consequence of working in shifts. In case of the usual constraints, the task can be expressed as an MILP (mixed integer linear programming) problem, where

integer variables are applied to decide on the existence of or opening the plants, on the manufacturing lines inside the plants, and on the number of necessary shifts in each plant.

The logic or binary decisions are usually treated with some special techniques, like Big-M, Multi-M, or Convex Hull. I have also found the Türkay and Grossmann model [3] for discontinuous cost functions.

The models found in the literature usually do not consider stepwise constant functions. Neither do they utilize the tendency of costs to monotonously increase, that is more shifts are specifically more expensive. Initialization is also difficult with the literature models. I developed a new model that utilizes the main characteristics of the presented problem class, but is not too specialized that would prevent it from being useful in similar cases.

The new model has been tested on the multicommodity problem, originally formulated with logic constraints, of SABMiller Europe. The smallest problem to be solved contains approximately 5000 to 6000 variables, among which 60 to 80 are binary, and 3000 to 4000 constraints of either equality and inequality type. The problems are solved with GAMS/CPLEX. Effectiveness of the different models on this problem are compared in Table 2. The largest problem solved by our model contained 670.000 equations and 1.280.000 variables, among which 875 were binary.

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Heterogeneous Catalytic Asymmetric Hydrogenations

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Asymmetric syntheses can be carried out with heterogeneous catalysts. In hydrogenations the adding of chiral compounds to the reaction mixture can result in enantioselective effect. Adding these compounds in catalytic amount, they are called chiral modifiers.

There are two systems of reactions known to result in almost total optical purity: hydrogenation of β-keto esters on Raney-Ni catalysts modified with tartaric acid, and hydrogenation of α-keto esters on platinum catalysts modified with cinchona alkaloids.

Such effects are highly specific to the reactant, chiral modifier and catalyst, as it is found in enzymatic reactions.

Research on asymmetric heterogeneous catalytic hydrogenations has been carried out at the Department of Chemical Technology for more than twenty years. Two model-reactions are used: reduction of the carbonyl group in ethyl pyruvate on modified platinum catalysts, and hydrogenation of the C=C bond of isophorone on modified palladium catalysts. Experiments have two aims: to achieve higher enantioselectivity and to get more insight into the behaviour of these systems, so as to help discovering new, effective methods.
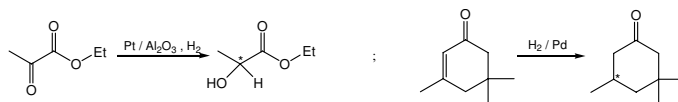
In this work, syntheses and tests of new, potential chiral modifiers have been made.

One part of the experiments is aimed at compounds synthetized from (S)-Proline. (S)-Proline derivatives such as $(S) - \alpha,\alpha$-diphenyl-2-pyrrolidinemethanol (DPPM) and $(S) - \alpha,\alpha$-dinaphtyl-2-pyrrolidine-methanol (DNPM) [1], esters and amides [2] result in reasonable enantiomeric excess. Also (S)-Proline can act as chiral auxiliary in some reactions, in diastereoselective hydrogenation of isophorone it is added in stoichiometric amount to the reaction mixture [3]. Studies of reaction mechanism appointed that formation of N-(3.3.5-trimethyl-cyclohexyl)-(S)-proline also occurs during the reaction. Therefore the reductive alkylation of (S)-Proline with the substrate itself, may provide products, which work as chiral modifiers in hydrogenations.

Another research topic is the use of [1,1']binaphtyl-2,2'-diols and diamines as chiral modifiers. These compounds have been examined thoroughly in homogenous catalytic processes and the [1,1']binaphtyl-2,2'-phosphates were considered usable, although they had not been examined in heterogenous reactions. Their common property is the axial chirality, that do not correspond to criterias to work as chiral modifiers in heterogenous catalysis. However, their effectiveness in homogenous reactions justified their investigations.

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Modelling Hybrid Extractive Systems with Interval Arithmetic Computations

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Due to the new challenges of economy and environment protection, hybrid processes are widely used in chemical industry. My research work specializes on batch extractive distillation and batch extractive stripping. The set of applicable mixtures and the set of applicable parameter domains of these processes can be determined with feasibility studies. The feasibility study methodology includes solution of differential algebraic equation systems (DAEs) that describe the process followed by an analysis of the phase portraits (profile maps). The target of the study is to find proper composition and parameter domains, in which the specified product composition can be reached from the temporary still composition. This includes the selection of the adequate part from the whole solution space. The boundaries of a feasible domain consist of the fixed points of the DAE and the separatices connecting them; in some cases other special solution curves (profiles) are also involved. The exact and reliable computation of these elements is very important.

I showed at the last conference that in case of batch extractive distillation the feasibility studies can be made more precise with computation of the fixed points; the loci of the fixed points change as a function of the parameters and at some parameter values bifurcations occur; the limiting parameters (limiting flows) can be determined using these values.

One of the research fields of our department is batch extractive stripping. This is a new separation method in which the mixture is charged to the top vessel of the column, and is separated with an extractive agent continuously fed somewhere into the column. The fixed points of the process-describing DAE and their change can be determined using reliable computation in the composition space in function of the parameters.

Although exact parameter values can be computed with the analysis of the fixed points and the bifurcation points, we only get approximate information about the feasible composition range of a given parameter value. Exploring the boundary-forming separatices is usually complicated because these solution curves connect fixed points.

In case of ternary systems, a separatrix may connect a node to a saddle point. In an infinite small neighbourhood of the fixed point the direction of the separatrix coincides with an eigenvector of the fixed point. Whether a solution curve in the neighbourhood of a fixed point approaches it or not is determined by the eigenvalues of the fixed point. If the exact loci, eigenvalues, and eigenvectors of the fixed points are known, and if the solution curve is eligible smooth, then the separatrix can be computed.

In practice, this is not realizable with real arithmetic computations. Use of reliable computations, on the other hand, guarantees that every solution box contains the true solution. The separatrix should be computed from the saddle because the solution curves start in the neighbourhood of the saddle, and end in the neighbourhood of the node. Reliable methods are needed for the computation because only these methods guarantee that every solution box contains a point of the real separatrix.

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Corn Fiber as Substrate for Hemicellulose Isolation and Ethanol Fermentation

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Corn fiber could be a perfect raw material for ethanol production in Hungary considering its amount and its degradability. The aim of the present investigation was to find out whether alkaline chemicals were efficient enough in breaking down the tight association between carbohydrates and lignin, thus enhancing enzymatic digestibility. NaOH and KOH solutions have been used in 1-2% concentration for the chemical treatment. According to the results the alkaline pretreatment of corn fiber has a great potential, since the obtained hemicellulose polymer is a highly valuable product [1-2] and can be recovered with 1 and 2 w/w% alkaline solutions at high yields (about 80%). Moreover, residual fibrous material, a well pretreated lignocellulosic raw material, is a potentially good carbon source for ethanol fermentation [3]. It could be hydrolysed by cellulases and the fermentability of the hydrolysate gave good results. The achieved ethanol yields were about 90% of the theoretical, which are highly above of that obtained with the reference substrates (Untreated corn fiber and Solka Floc: delignified cellulose pulp).

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Investigation of Resistant Starches

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Resistant starches (RS) can be applied in food industry in order to reduce the glycemic index (GI) of products.

Glycemic index measures the amount and kinetics of liberated glucose during enzymatic digestion. Food products with reduced GI can be used in the therapy as well as in prevention of obesity and diabetes mellitus (type II) as well as weight management.

The aim of the present study was to investigate the physical, chemical and functional properties of different resistant starches (origin, type of resistance) and their comparison with native starches in pure form and in stoichiometric mixtures.

Measurements were carried out to determine the enzymatic digestibility, water absorption, thermogravimetric parameters (using differential scanning calorimetry=DSC) and viscometric characteristics (using rapid visco analyser=RVA) of resistant and native starches and their mixtures.

Enzymatic digestibility was reduced linearly by adding RS-s into mixtures. The changes of water absorption also showed linear relationship in RS-native starch mixtures.

The RVA parameters, which describe the functional properties of starches, have shown non-proportional character in the stoichiometric mixtures.
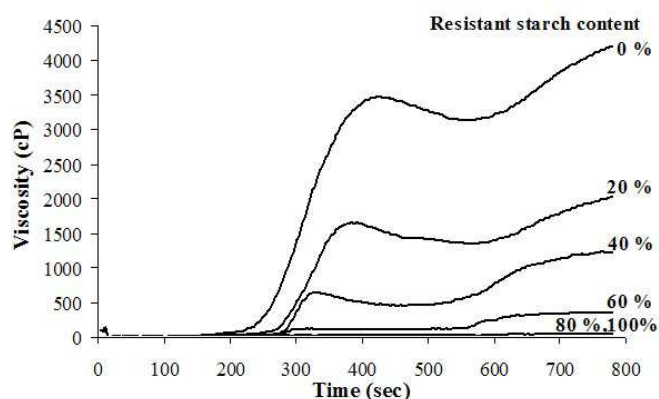

Fig. 11. Changes of the RVA Curves in the Wheat Starch and RS4 Mixtures

Five RVA parameters (peak viscosity, trough, breakdown, setback, final viscosity) were sensitive enough to follow the changes of functional properties in starch mixtures.

The results of DSC measurements proved that the gelatinizations of resistant starches are quite different and only type RS4 (chemically modified) is heat sensitive.

The enthalpy reducing effects of RS in mixtures were confirmed during gelatinization.

Based on the results two RS products were selected for development and innovation of food products with reduced glycemic index.

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## New Synthesis of 7,8-dimethoxy-tetralin-2-one

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2-Tetralones containing hydroxy and/or methoxy substituent(s) on the aromatic ring are known as important sources of synthetic precursors of a wide range of compounds, including steroids, heterocycles and pharmaceuticals [9]. The synthesis of 7,8-dimethoxytetralin-2-one (**1**) is described in the literature [2], most of the elaborated methods, however, use starting materials and reagents [3–5] that are not easily accessible and inconvenient, respectively. Additionally, in many cases poor or uncertain yields were reported [6–8].

2a; $R^1=R^2=H$
2b; $R^1=CH_3$, $R^2=H$
2c; $R^1=CH_3$, $R^2=CHO$
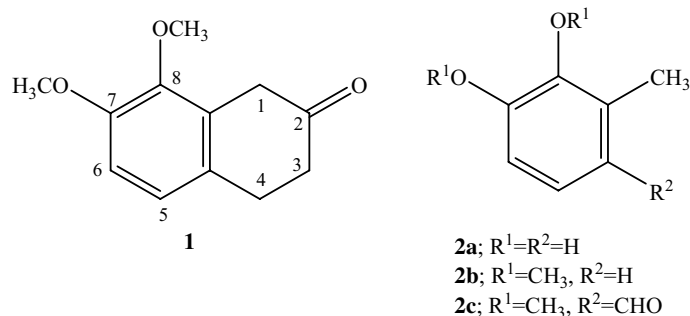
In my lecture I report an efficient methodology to synthesize the title compound (**1**) using simple reaction steps, commercially available starting materials and reagents [9]. Most of the reaction steps were carried out in 10-30 g quantities.

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Synthesis of Heterocyclic Compounds Using Zeolite Catalysts

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In the last years one of the important research projects at the former Department of Organic Chemical Technology of Budapest University of Technology and Economics has been the investigation of new acidic and basic heterogeneous catalysts for developing new, more environment-friendly syntheses. In the frame of this research work we checked whether a zeolite-type adsorbent family, Ersorb is applicable in various organic syntheses.

Ersorb-4 (E4) is a Ca-K mixed cation-based clinoptylolite-type zeolite material with 4 Å pore size [1]. It has a specific surface of 40 m^2/g. E4 has a slightly surfacial acidic character. It can adsorb small molecules such as water, hydrochloric acid, ammonia, methanol or hydrogen sulfide. Based upon this adsorption ability, E4 is used as large spectral drying agent (molecular sieve) in both gaseous and liquid phases.

E4a is the more acidic modification of E4. The original E4 was modified by ionic exchange to change the surface acidity of the material. Its pH is about 3.

We developed simple, cheap and environment-friendly syntheses of different heterocyclic compounds using these zeolites as catalysts. Thus:

– Aromatic carboxylic acids and 2-aminoalcohols gave the appropriate 2-aryloxazolines with good yield [2].

– In a similar way, the reaction of substituted benzoic acids with ethylenediamine yielded the appropriate substituted 2-phenylimidazolines with good yield [3]. We investigated the synthesis of the appropriate condensed heterocycles (benzoxazole and benzimidazole derivatives), too.

– *o*-Phenylenediamine and aromatic and aliphatic ketones gave substituted 1,5-benzodiazepines with good yield in the presence of E4a [4].

– The Biginelli reaction of aldehydes, ethyl acetoacetate and urea or thiourea resulted the formation of the appropriate 4-aryl dihydropyrimidinones [5].

– The Bischler-Napieralski reaction in the presence of E4 resulted isoquinoline derivatives with good yield [6].

– The Pictet-Spengler reaction of *β*-phenyl-ethylamines and aldehydes or ketones in boiling ethanol in the presence of E4a resulted 1-aryl-1,2,3,4-tetrahydro-isoquinolines in one step and high conversion [7]. The analogous oxa-Pictet-Spengler reaction of phenylethanol derivatives yielded 1-aryl-isochromans also with good yield [8].

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Qualification of Assessors in Food Profile Analysis

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Sensory quality is an important part of product potential, especially in food industry. Since sensory quality is perceived by human assessors, the subjective character cannot be totally eliminated, that is why designing and implementing sensory tests can be effectively aided by the application of Mathematical Statistics. By the evaluation of these tests we can not avoid applying the tools of modern Information Technology.

Profile analysis is one of the often applied laboratory tests that need trained assessors and/or experts (preferably a product specific panel) to take part. The reliability of this method is based on the reliability of the assessors, thus it is useful to qualify them in each profile analysis test.

The researchers of the Sensory Laboratory (BCU) and of the Department of General and Analytical Chemistry, Chemical Information Technology Group (BME), produced a profile analysis supporting software, the ProfiSens, that was applied in research and education, in the design and elaboration of profile analyses in hundreds of cases. The conclusions of these applications resulted in a new development, which offers a fast graphic way to investigate the reliability of panelists.
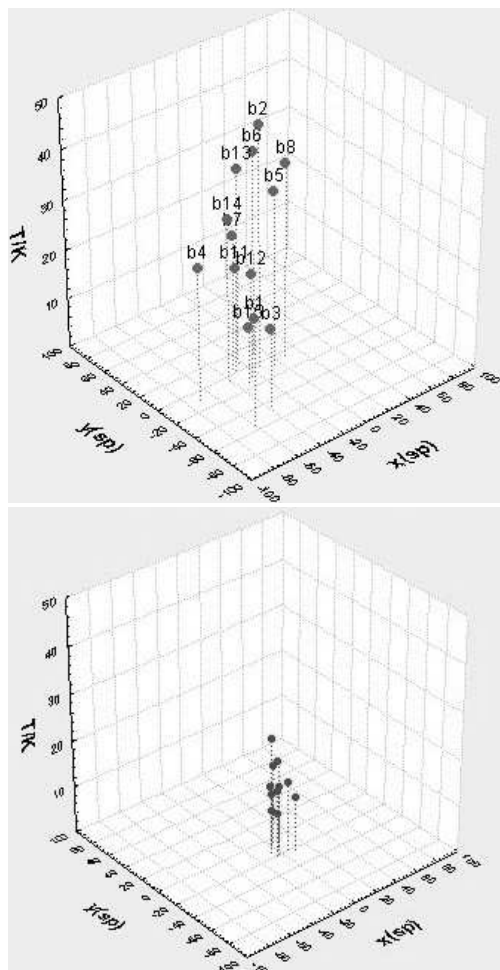
Fig. 12. Area / perimeter over gravity points of profile plygons belongig to a not reliable panelist group (left side) and to a reliable one (right side)

To get an overview on the reliability of a panel, it would be very tiresome to investigate the whole ANOVA tables of the ProfiSens for each attribute step by step. Our research team designed a new and fast graphic reliability test. The qualification is based on the fractal theory, which characterizes fractals by their area / perimeter ratio. Of course this ratio is not enough to describe a profile analysis polygon, because a rotation of a $k \cdot 2\pi / n (0 < k < n)$ angle of a profile polygon means exactly a shift of the assessment by k attributes. The exact characterization is offered by the area / perimeter ratio <u>and</u> the gravity centre of the polygon.

The coordinates of the gravity centre shown on Fig. 12 were calculated by our own extension of the ProfiSens software. This extended module adds new worksheets to the basic Excel workbook, that contains the numerical and graphical results of a food profile analysis carried out by ProfiSens, according to the number of samples. The new Excel worksheets contain the Cartesian coordinates of the profile polygon's gravity centre, and as third Cartesian coordinate the evaluated area/perimeter ratio of the polygon belonging to each individual panelist.

The created new test method improved the efficiency of research concerning the market potential of new fruit or vegetable varieties, new formulas or different treatments in food industry.

Investigation of Controllability of Systems with Recycle

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Nowadays, the cost-side approach and the tendency to increase the efficiency of processes have become the most important viewpoints, especially in cases when chemicals are produced in large amount by separating processes. Separation of liquid compounds is often achieved by recirculation, augmenting the importance of the two previously mentioned conditions. The recirculation as a procedure compiled by process-design is worth investigating from several points of view; it is not only an important member of the whole process, it can dramatically change the properties of the system.

In the course of my work I investigate the advantageous and harmful effects of a recycle applied in an industrial separation system and the opportunities to decrease the harmful ones. In order to achieve this I compared the system with recycles and without recycles, both in the steady state and dynamic range. The system product is ethylbenzene. It contains a reactor and three distillating columns. In the steady state range the system is described by the controllability indexes (CN, MRI, RGA and NI), while in the dynamic range it is characterized by the step responses of different disturbances and the parameters from the identifications of these curves. The goal is to design different control loops that give opportunity to eliminate the harmful effects of the recycle and to guarantee a reliable separation corresponding to the purity requirements of the product.

The system with recycles:
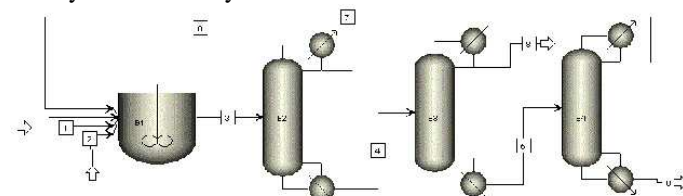
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Relationship between NIR and RVA "Spectra" in Germinated Wheat

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Near infrared (NIR) spectroscopic methods are widely used in the determination of chemical composition and quality of wheat. The NIR spectra include both chemical and physicochemical or physical information of materials tested.

Rapid Visco Analyser (RVA) method is a sophisticated determination method describing the rheological properties (viscosity against time and temperature) of wheat meal/flour-water slurry. The RVA curves can also be interpreted as a physicochemical "spectrum" of the material.

During germination significant biochemical changes occur, due to the mobilization of seed reserves by enzymes.

The aim of the study was to find out whether the early phase of germination process could be detected by the rapid methods mentioned above. The relationship between NIR spectra and RVA curves of wheat samples during the seed germination procedure was also investigated.

The germination (in a period of 0–72 hours) has significant effects on the viscosity curves and from the seven characteristic RVA parameters (peak viscosity, trough, breakdown, final viscosity, setback, peak time, pasting temperature) the breakdown can be used for sensitive detection of early germination.
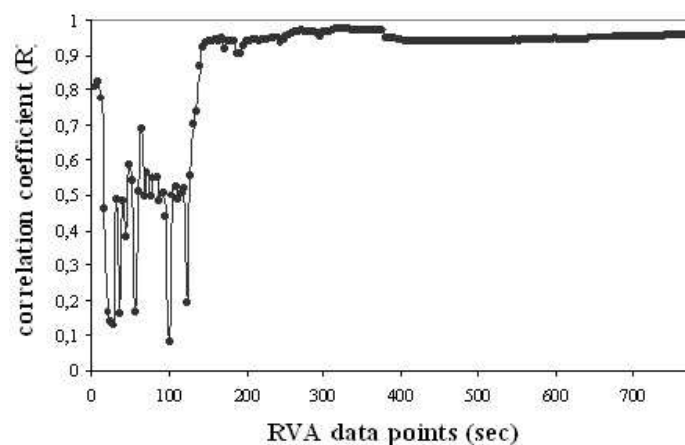

Fig. 13. PLS (Partial Least Squares) correlation coefficients between predicted values based on full range NIR spectra of wheat samples and viscosity values measured by RVA

Four RVA parameters (peak viscosity, trough, final viscosity and setback), as reference data, showed high correlation coefficients ($R = 0.950$–0.970) with NIR reflection spectra. Viscosity data of RVA curves between 220–340 seconds showed the most characteristic change during early heat treatment of the pasting procedure. It was also pointed out that there is a high correlation between NIR and RVA data beyond this period of time (Fig. 13).

Results indicated that NIR spectra can be used for rough prediction of some RVA parameters with acceptable accuracy and rheological quality could be predicted by NIR fast and non-destructively.

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Comprehensive Investigation of Energy-Integrated Distillation

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Distillation is a key separation technology in chemical industries for the separation of liquid mixtures. The disadvantage of distillation is its high energy consumption that involves high operating cost for these separation units. Significant energy savings can be reached with the use of distillation structures applying energy integration such as heat integration, heat pumping and thermocoupling.

In this work different energy-integrated distillation schemes are investigated and they are compared to each other and to the conventional arrangement in case of ternary mixtures. The comparison is based on economic features and operability. Dynamic behaviour of the distillation schemes is also investigated.

The studied distillation schemes are:

- Heat-integrated distillation scheme with backward heat integration. The base idea of this distillation system is to use the overhead vapour from the second column to provide heat to the first. The reboiler of the first column is combined with the condenser of the second (Fig. 1).

- Petlyuk column, also called fully thermally coupled distillation column, consists of a prefractionator and a main column. The required heat amount for the separation is provided through direct contact of the material flows (Fig. 2).

- Sloppy distillation system with forward heat integration. This distillation system basically is a heat-integrated sequence, but in the prefractionator sloppy separation takes place. There is no material flow from the main column to the prefractionator (Fig. 3).

- Side rectifier column is a partially thermally coupled distillation system. A rectifier is connected to the main column (Fig. 4).

- Side stripper column is another partially thermally coupled distillation system. The head product of the main column contains the most volatile component, the middle component is purified by the side stripper and the bottom product contains the heaviest component (Fig. 5).

Conventional direct distillation scheme is used for comparison. It consists of two simple distillation columns connected in such a way that the bottom product of the first column is the feed of the second column. In the literature, they are considered to be conventional arrangements for ternary distillation. (Fig. 6).
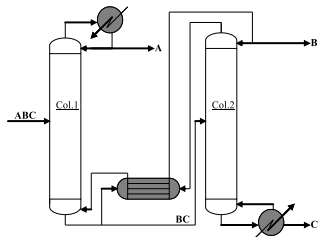

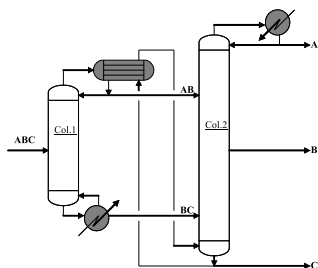**Fig. 14.** Heat-integrated distillation scheme with backward integration
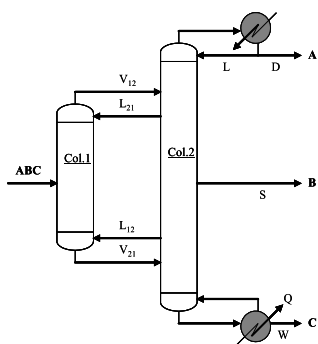

Fig. 15. Petlyuk column

Fig. 16. Sloppy distillation scheme

Investigating economic features of the distillation systems three different ternary mixtures are studied and three product purities are expected (*Table* 1-2).

Tab. 1. Ternary mixtures studied

Mixtures		
1.	pentane	hexane	heptane
2.	isopentane	pentane	hexane
3.	butane	isopentane	pentane

Tab. 2. Expected product purities

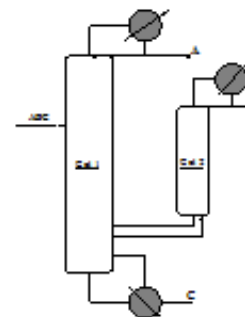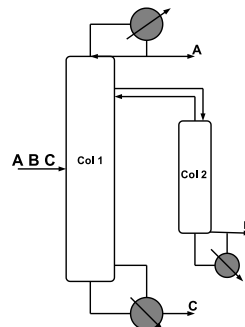| Case	Product Purities (%)
1	99
2	95
3	90

Fig. 17. Side rectifier column

Fig. 18. Side stripper column

Distillation systems are studied by rigorous modelling made by ASPEN and compared to each other on the basis of total annual cost. Energy-integrated distillation systems are always better than the conventional structure. The heat-integrated systems are the most economical arrangements, and they are almost always better than thermally coupled distillation systems.

Dynamic simulations are carried out to investigate the dynamic behaviour of the energy-integrated distillation systems and to find the best control structure for them.

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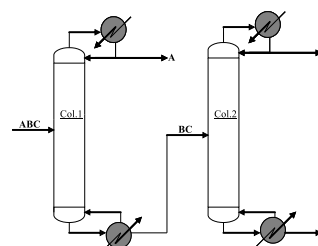
Fig. 19. Conventional distillation scheme

Analysis and optimization of hybrid separation systems based on pervaporation

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Pervaporation is one of the newest and most developing membrane technologies and it has the advantage that it can be used for special separation tasks. It may be successfully applied for the dehydration of organic solvents, the recovery of organic compounds, and the separation of organic mixtures depending on the type of the membrane. Currently, about one hundred pervaporation units are operating world wide, most of them dehydrate various solvents, such as ethanol and isopropanol [1, 2].

The advantages of a pervaporation process can even be increased if it is combined with other separation prosess(es), *e.g.* distillation, thus a so called hybrid separation process is formed. In this work hybrid separation systems (combination of distillation and pervaporation) are analysed. Three schemes are investigated:

1 pervaporation followed by distillation of the permeate stream (PV+D)
2 distillation followed by pervaporation (D+PV)
3 distillation followed by pervaporation and another distillation (D+PV+D)

To simulate the pervaporation a special subroutine is written based on the solution-diffusion model [3] in the frame of the ChemCAD software. Laboratory pervaporation experiments and literature data [4] define the parameters of the selected solution-diffusion model. The hybrid processes containing PV and D are optimized and the required membrane area is defined.

The three separation schemes are simulated and compared on the basis of an industrial hybrid separation process separating ethanol and water. The feed is 800 l/h mixture of 1 bar and 60°C containing 80 v% ethanol and 20 v% water. The aim of all the three processes studied is to obtain ethanol with a final purity of 99.7 wt% and almost ethanol free (min. 99.9 wt%) water.

The total annual costs (TAC) are determined. According to the rigorous simulations the most economic hybrid process for this separation problem is the distillation followed by series pervaporation (D+PV).

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Interaction of aromatic molecules with hydrogels containing peptide bonds

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Intelligent soft materials have recently emerged as a topic of intense research activity as their potential is recognized for replacing or acting as substrates for biological tissues or as sensors of biomedical or environmental signals. The operating principle of such devices relies on materials whose volume changes abruptly, *i.e.* displays a volume phase transition (VPT), when an appropriate stimulus is applied. Poly(N-isopropylacrylamide) (PNIPA) is a material that is widely used for this purpose since its VPT in pure water is at a temperature convenient for many applications, close to 34°C. Despite the abundant literature on PNIPA, however, the mechanism of the transition and the thermodynamic parameters governing the phenomenon are incompletely understood, particularly in the collapsed region immediately above the VPT. Knowledge of material properties in the vicinity of the VPT is essential for any application working in this temperature range.

The interaction between aqueous phenols and PNIPA also has biological relevance. Owing to the C(=O)-NH- bonds, the polymer chain of the PNIPA can be considered as a model protein, while phenyl is a frequent substituent of amino acids or other biologically active molecules [1].

Our research on a phenol-sensitive device for sensor and/or adsorption applications yielded results that are difficult to interpret in terms of the current literature. We therefore undertook a systematic investigation of the unidentified interaction of phenols with PNIPA hydrogels by applying a multi-method approach. The observations reported here involve measurements of swelling degree, aromatic uptake, isothermal microcalorimetry, dynamic light scattering (DLS) as well as small angle neutron scattering (SANS).

The equilibrium swelling ratio of PNIPA gels is modified in the presence of phenols. At a critical aromatic level, influenced by the number of OH-groups decorating the benzene ring, a phase transition occurs already at 20 °C that is much more abrupt than in pure water (Fig. 20 $1/\phi_e$, where ϕ_e is equilibrium swelling ratio of the polymer).

The phenol uptake of the gel is comparable to that of activated carbon (1.02-1.9 mmol/g dry gel) [2]. Unlike classical adsorption the shape of the isotherms and the sorption capacity is primarily determined by the number of the OH-groups.

According to the results of the microcalorimetric investigations the phase transition is preceded by an exothermal structural change at a concentration significantly lower than that of the first order phase transition.

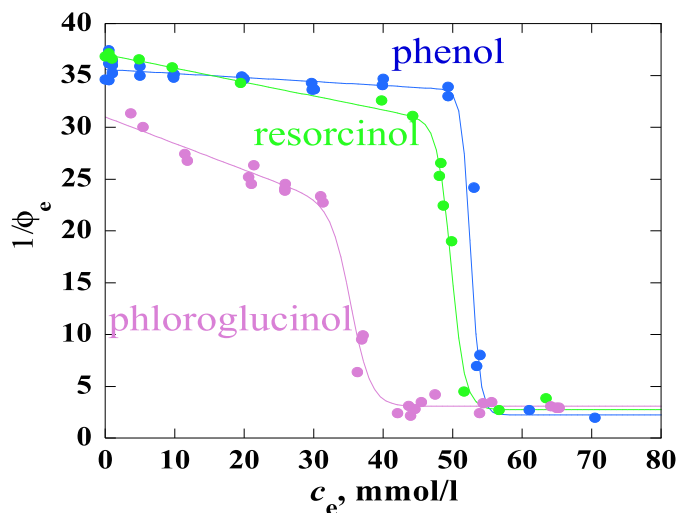DLS and SANS experiments confirmed that the aromatic

Fig. 20. Effect of the phenol, resorcinol and phloroglucinol concentration on the equilibrium swelling of the PNIPA gel at 20 ˚C

molecules practically do not establish a binding relationship with the polymer. It is probable that the phenol molecules are located in the aqueous region among the hydrated polymer chains [3].

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The relationship of primary and ascorbic acid metabolism in plant mitochondria

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Ascorbic acid is the most important water-soluble antioxidant in animal and plant cells and also a co-factor for several enzymes. Due to mutations in the enzyme catalysing the last step in the synthesis, humans and a few animal species are unable to synthesise it, we cover our need from plant sources. Surprisingly, the biosynthetic pathway in plants has only been elucidated recently. Mitochondria play an essential role, since the enzyme catalysing the last step is located in the inner mitochondrial membrane [1], coupled to the mitochondrial electron transfer chain. Sufficient level of ascorbate is not only maintained by *de novo* biosynthesis but also by the reduction of oxidized ascorbate produced in different reactions [2]. Recycling of the oxidized form dehydroascorbate into ascorbate was first described in chloroplasts. The electrons required for

the reduction of dehydroascorbate come from NADPH via glutathione. The enzymes of the reduction cycle were found in mitochondria as well. The recently described mitochondrial ascorbate/dehydroascorbate transporter [3] and the mitochondrial presence of enzymes contributing to reduction of dehydroascorbate suggest that besides *de novo* ascorbate synthesis mitochondria plays a major role in sustaining the redox status of ascorbate [4].
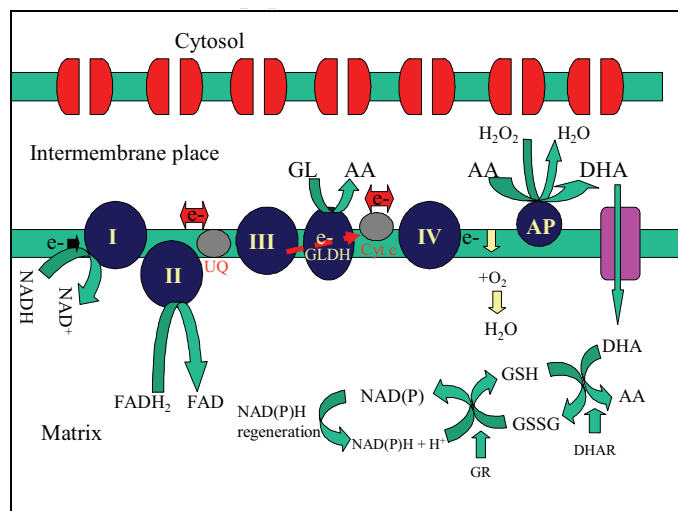

Fig. 21. The hypothetical relationship of mitochondrial respiration and ascorbic acid metabolism

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Sythesis and optical investigation of 1,1'-binaphtho(aza)crowns carrying photochromic signalling unit

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Photochromic materials have attracted much attention in the last decades because of their potential applications as optical fibres, switches, optical memories and other molecular devices. The photochromic behaviour of spirobenzopyrans was discovered for years ago. These type of molecules have since become one of the most extensively studied group of photochromic materials. Upon UV irradiation, the colourless spiropyran is trans-

formed to the coloured merocyanine. The process can be reversed either thermally or by irradiation with visible light.

Interestingly, chiral crown-spiropyran conjugates have not been reported, although the photochromism of these receptors may be affected by chiral ammonium salts and amino acid derivatives.
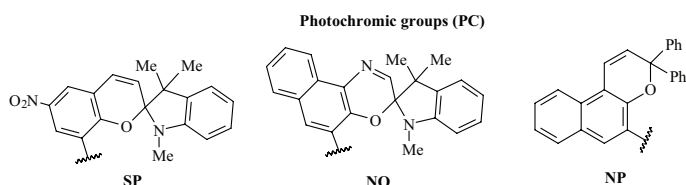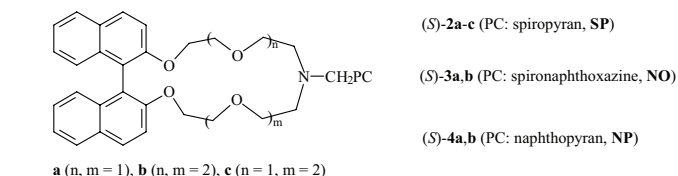

(S)-**2a-c** (PC: spiropyran, **SP**)

(S)-**3a,b** (PC: spironaphthoxazine, **NO**)

(S)-**4a,b** (PC: naphthopyran, **NP**)

a (n, m = 1), **b** (n, m = 2), **c** (n = 1, m = 2)

Photochromic groups (PC)

SP   **NO**   **NP**

Fig. 22.

Our main goal was the synthesis of the first photochromic molecules based on chiral crown ethers. We expected our molecules to show enantiomer-dependent photoisomerisation upon complexation of chiral ammonium ions. (S)-1,1'-Binaphthol-derived azacrowns bearing different photochromic moieties and different ring size were prepared. The photochromic groups were as follows: spirobenzopyrans (**SP**), spironaphthoxazines (**NO)** and naphthopyrans (**NP**). First of all, the photochromic behaviour of our molecules were studied by UV/vis spectroscopy in the presence of alkali and alkaline earth metal ions. The **SP**-ligands were transformed to the coloured merocyanine form even under dark conditions. The spiropyran-merocyanine equilibrium was affected by the binding ability of the crown rings and by the strength of ionic interactions between the merocyanine phenolate anion and the metal cation.

The photoisomerization of crowned spironaphthoxazines under dark conditions was affected by only Ca^{2+} and Mg^{2+} ions, while the spectra of the naphthopyran ligands did not change under the same conditions. However, upon UV irradiation the isomerization took place and the absorption maxima of the new bands were dependent on the cations used. Preliminary investigations with chiral ammmonium compounds indicated some enantiomer recognition, which will be studied in details in the Department of Physical Chemistry.

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The sodium transport in polycrystalline alumina

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In the high pressure sodium lamps the light is emitted from a sodium containing gas discharge zone, which is maintained in a polycrystalline alumina tube [1]. The arc tube has to resist the hot sodium vapours in the lamp, even at elevated temperatures during the operation. Sodium loss occurring during the operation is one of the most important processes that influences the lifetime of the lamp. Due to the loss of the sodium the composition of the sodium amalgam dose changes, hence vapour pressures of sodium and mercury change in the discharge, resulting in burning voltage increase and the successive switch off of the lamp [2].

The scope of our work was to study the sodium transport through the ceramic arc tube. A high amount of sodium can be detected by X-ray Photoelectron Spectroscopy and Secondary Ion Mass Spectroscopy on the external surface of the ceramic discharge tube and on the internal surface of the glass outer bulb of long-aged lamps. The transport through the ceramic arc tube consists of more steps (solution in the ceramics, diffusion through the ceramics, leaving the bulk phase, evaporation from the surface). Among the listed processes the mechanism of the diffusion was investigated by model-experiments. A ceramic arc tube was applied as a reactor chamber, in which polycrystalline ceramic plates were heated at 600-1100°C in controlled Na and Xe atmosphere. Sodium diffusion profiles in polycrystalline alumina developed by the heat-treatment were measured by XPS and SIMS.
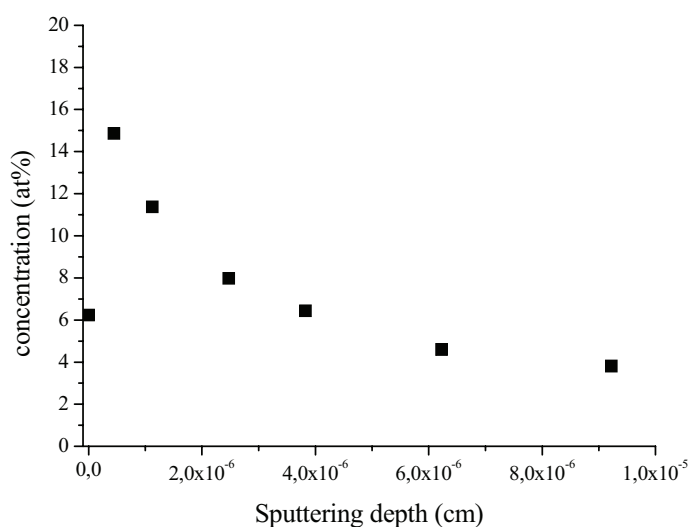

Fig. 23. The sodium diffusion profile in a polycrystalline Al_2O_3 Heat-treatment: 1100°C/0.5h

From the measured concentration profiles we concluded that the grain boundary diffusion plays an important role in the formation of the sodium diffusion profile. Among the three types of grain boundary diffusion kinetics described by Fischer's model, type B determines the sodium concentration profile in this polycrystalline ceramic at high temperatures and in deeper layers. This is an intermediate case, there is simultaneous diffusion in the volume, starting from the surface, and along the grain boundaries. The sodium loss in HPS lamps fundamentally occurs with the mechanism of the abovementioned type B of grain boundary diffusion. However, other processes could have influence on the diffusion, for example the intensive light flux under lamp conditions.

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Complex activity of clay and CNT particles in flame-retarded EVA copolymer

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Metal hydroxide (MH) active fillers are the most widely used flame retardants. Recently these fillers have been combined with nano-fillers of very high specific surface area [1]. The importance of interface modification promoting better dispersion is quite obvious in these systems. The interfacial layers affect the mechanism of flame retardancy in a complex way: homogenity, charring, transport processes, thermal and mechanical stabilities of the systems can be influenced. The role of active metal ions, occurring at the surface of fillers, in flame retardancy and other stability features has been studied in this work.

Confocal Raman microscope was used to analyse the degradation locally at the neighbourhood of nanotube and clay additives. The double-walled carbon nanotube (DWCNT), containing Co catalyst residue, accelerate the deacetylation process of ethylene-vinyl acetate copolymer (EVA) considerably, while the montmorillonite (MMT) has no significant influence under static circumstances. The compounding process influences the effect of MMT, causing partial crosslinking in EVA during the compounding. This mechanochemical reaction is catalyzed by uncovered MMT particles, while organophillized MMT (OMMT) promotes rather the charring process. Inorganic surface modification with various metals also has some stabilizing effect. Spray drying of MMT results in microparticles of increased surface area and improved thermal stability of EVA systems. The lowest rate of flame spreading was achieved using uncoated MMT, while the coating with cationic surfactant was most efficient for hindering the dripping.
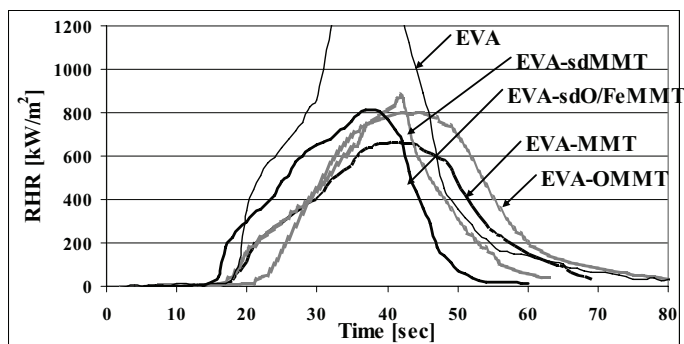

Fig. 24. Rate of heat release (RHR) curves of EVA and various EVA-MMT systems at 50 kW/m^2 heat irradiation

The rate of heat release (RHR) of the organically modified (EVA-OMMT) and the spray dried MMT (EVA-sdMMT) was approximately the same. The combined organically/inorganically modified clay moderates both the dripping and the flame spreading in EVA [2].

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Synthesis of new achiral and enantiopure chiral monoaza-18-crown-6 ether type PET sensors

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Starting from relatively cheap and commercially available materials new achiral and enantiomerically pure chiral PET (photoinduced electron transfer) sensors (see Figure) were synthetized by multistep reactions.

Photoinduced Electron Transfer (PET) sensors are molecular fluorescent switches that can translate the act of capturing a chemical target (guest) by a receptor (host) into an easily comprehensible light signal from a fluorophore. This type of sensor molecules have a modular structure of three parts: fluorophore - spacer – receptor [1].

Acridone derivatives have an intense fluorescence, so we designed PET sensors having acridone units as fluorophore moieties attached by a methylene spacer to monoaza-18-crown-6 ether type receptors.

These new PET sensors are intended to be used in selective sensing of biologically important cations and the enantiomers of protonated chiral primary amines.

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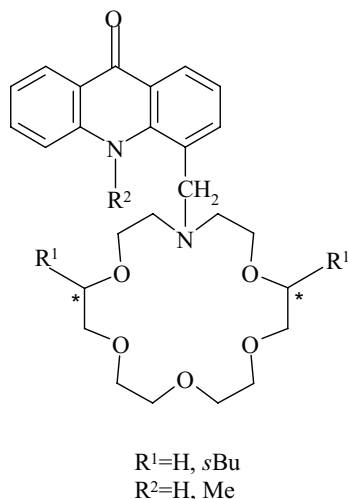
R¹=H, sBu
R²=H, Me

Fig. 25. New achiral and enantiopure chiral PET sensors

Resolution by supercritical extraction, the effects of process parameters

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Besides several cumbersome ways of enantiomer resolution, one of the most important advantages using supercritical fluid extraction methods are the possibility of creating fast and environmentally green separation processes.

The effectiveness of the separation procedure can be influenced by numerous factors during the different steps of the separation (diastereomer formation, extraction, diastereomer decomposition). For instance, resolving racemic ibuprofen ((±)-2-(4-isobutyl-phenyl)-propionic acid, IBU) with $R - (+)$-phenylethylamine (PEA), the quality of the solvent and the resolving agent have significant effect on the extraction curves and the resolvability (F);

$$F = ee_{extract} \cdot Y_{extract} + ee_{raffinate} \cdot Y_{raffinate},$$

where ee is the enantiomeric excess, Y is the yield of ibuprofen regarding to the amount of the raceme compound (Fig. 26) [1]

Additionally, the pressure and temperature of the supercritical solvent as operational parameters have also significant influence on the efficiency of the enantiomer separation and on the enantiomeric excess. Resolving the complex molecules of *trans-2-halogene-cyclohexanols* using (−)-dibensoyl tartaric acid as resolving agent, according to the strong pressure and temperature influence, the complexes can be *in situ* decomposed at a certain pressure and temperature. Therefore the enantiomers can be fractionated and retrieved directly [2].

Optimizing the several factors of the resolution methods using supercritical fluid extraction, effective and environmentally safe technologies can be developed.
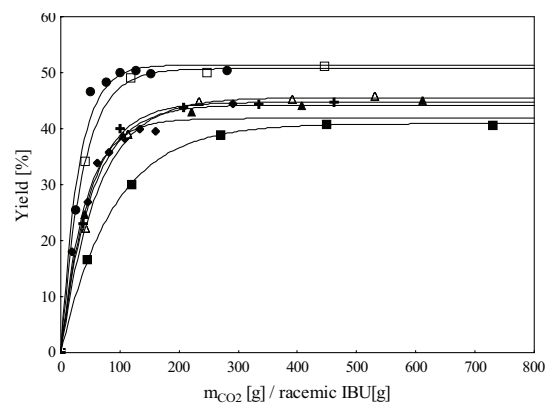
Solvent	F
◇ Acetone	0.427
□ Tetrachloro methane	0.403
● Dichloro methane	0.404
▲ Ethyl-acetate	0.362
■ Ethanol	0.353
△ Methyl-ethyl-keton	0.354
Methanol	0.381

Fig. 26. Extraction of unreacted (S)-(+)-IBU using different solvents at the sample preparation. Reached resolvability

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Development of Continuous Measuring Method for Adsorbable Organically Bound Halogens in Waters (AOX Monitor)

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AOX = **a**dsorbable **o**rganically bound **halogens**.

This measuring procedure can determine the chlorine, bromine and iodine content in the adsorbable organic components (organic fluoro compounds can not be measured this way).

AOX is a very dangerous material group because it has toxic, mutagenic, and carcinogenic effect and strong bioaccumulation property in fat containing tissues. They are generated in almost every reaction of organic substances and reactive halogens (even in household cleaning by hypochlorite containing fluids). The reaction products can go through the waste water treatments to the rivers and lakes. Thus, we have to measure it not only at the

end of pipes, but in rivers and lakes too. Even if there is a clean water source not polluted by industrial effluents, its organic trace components will produce AOX components when the required chlorination (desinfection) is applied before usage in a tap water pipe-line network.

Up to date there is no any continuous mesaurement method of AOX. We do not have any realtime data on the amount of AOX what we are drinking day by day.

A laboratory method is known, however, that takes long time and is a complicated measuring procedure. There is a standard describing of this measuring method.
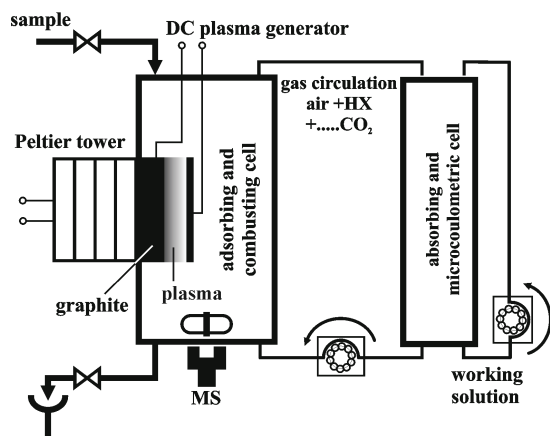

Fig. 27. Theoretical AOX monitor

We have studied this procedure and designed a revolutionary new technique to establish a miniaturized and automatizable method, which is principally a variation of the standard method. In this invention we introduce a novel, miniature and very effective plasma incinerator process that runs with low power consumption and uses ambient air instead of noble gases. The electrochemical detector is also redesigned to fit to the small sample amount used in the absorption unit.

Our instrument has two parts, a microcoulometer (that can absorb the halogen-acids coming from the incinerator unit), and an incinerator cell [1, 2].

While the laboratory microcoulometer can measure 0,1 μg to 300 μg chloride, our microcoulometer can measure near *500 pg* chloride.

The target specifications for the prototype AOX Monitor are:

- Measurement frequency: 1-6 measurement/hour (depends on concentration)

- Measuring range: 0,1-1000 μg halogen/litre water

- Unattended period: 7 days

References

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Determination of the Photolysis Quantum Yield of 2 Butanone and Acetone- d_6 Using Exciplex-Laser Photolysis

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Acetone is the third most abundant volatile organic compound occuring in the Earth's atmosphere. Its photolytic decomposition is one of the most important HO_x sources in the upper troposphere. We have developed a pulsed-laser photolysis/gas-chromatographic analytical method (LP/GC) that can be applied with good results for the determination of consumption quantum yields (Φ) of carbonyl compounds. Previously, applying this method, we have determined Φ for acetone at several reaction temperatures and pressures and in the presence of various buffer gases [1]. These results show an unusual pressure and temperature dependence in accordance with a very recent literature. Thus, we have applied our LP/GC method for studying other systems.
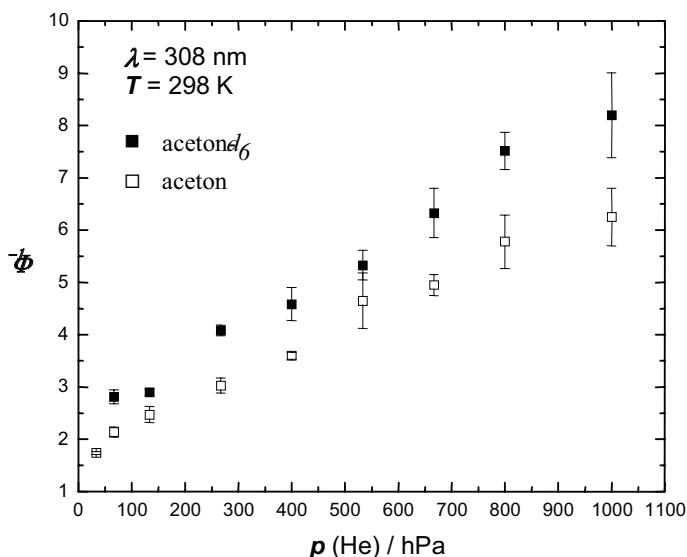

Fig. 28. Pressure dependence of the photolysis quantum yield of acetone-d_6 and acetone in He buffer gas

There are only a few data available in the literature concerning the photolysis of deutero-acetone ($CD_3(CO)CD_3$) and methyl-ethyl-ketone ($CH_3(CO)C_2H_5$). As a first step in our study, we have measured the UV absorption cross-section of these molecules using conventional spectrometric method. In the next step, applying the LP/GC method, the photolysis quantum yields were determined at room temperature at different pressures and with different buffer gases. The results obtained for acetone-d_6 are shown in Fig. 28 in Stern-Volmer representation. The photolysis quantum yield for acetone-d_6 is significantly smaller than that of acetone, which may indicate an increased role of internal conversion.

The following consumption quantum yields for 2-butanone photolysis have been determined in synthetic air at room temperature: 133 hPa: 0,79 $\pm$ 0,01, 400 hPa: 0,65 $\pm$ 0,02 and 667

hPa: $0{,}42 \pm 0{,}01$. These Φ values agree satisfactorily with the IUPAC recommendation, but the recommended value is based on a limited number of determinations.

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Modelling of Extraction of Corn Germ

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Modelling of extraction is highly desirable when a production plant is designed. With the model, the optimal particle size, residence time, solvent flow, temperature and pressure can be determined. Additional data from pre-experiments help to plan the extraction process. In this work the modelling of the Soxhlet- and the supercritical fluid extraction was studied.

In case of Soxhlet-extraction a set-of differential equations were obtained from the mass balance [1]. Solving these equations the dimensionless concentrations in the raffinate and extract were determined in function of time. A computer program was completed to minimize the sum of the absolute error between experimental and calculated concentration values. The parameters of the differential equations were; factor from the constants of the Fick I. equation (ν), liquid ratio (f), and solvent flow (W_E) divided by the quantity of raffinate (R). The f and the W_E/R values were calculated from experimental results, therefore only the ν factor was fitted.

A computer program based on the works of Sovová [2, 3] was completed to describe the supercritical fluid extraction. The extraction yield curves were measured and cut off experiments were carried out. The raw material was divided into 10 equal parts and after the cutting off experiments the remained oil concentrations in the raw material matrix were determined by traditional laboratory Soxhlet-extraction with n-hexane. The dimensionless model parameters were obtained by curve fitting, other data (density of the fluid, solubility of oil in the fluid, specific surface area of raw material) were determined from empirical equations. The initial concentration, the raw material density, and the void fraction in bed were obtained as a result of laboratory experiments. The mass transfer coefficients in the fluid and the solid phases were determined using the parameters mentioned above. Typical extraction and concentration curves are shown in Fig. 29.

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The Enantioselective Synthesis of α-aminophosphonates

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α−Aminophosphonic acids as the isosters of amino acids have growing importance both as biologically active compounds and as complex forming agents. It has been shown that the biological activity of α-aminophosphonic acids is influenced by the absolute configuration of the α-carbon [1]. In the last decades numerous synthetic methods providing raceme α-aminophosphonic acids have been developed, but only a few stereo selective methods have been elaborated up to now. The most frequently used approach is the phosphorylation of imines by dialkyl phosphites. I present here our results on the catalytic enantioselctive version of the imine phosphorylation.
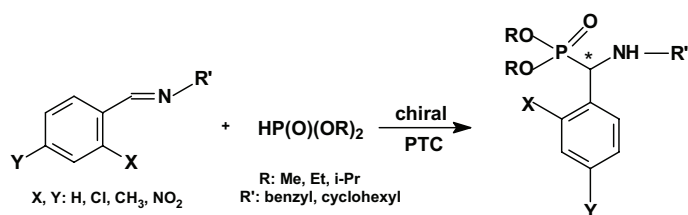

Fig. 30.

As the α-aminophosphonates can be prepared by phase transfer catalytic method [2] our first goal was to check whether chiral induction could be generated by chiral phase transfer catalysts.

At first, chiral crown ethers having sugar moiety have been used. We found that the strength of the base was decisive on the outcome of the reaction as using strong base numerous byproducts formed. Using weaker bases such as BaO and KF only the desired phosphorylation occurred with low-medium enantioselectivities (2-52% ee). The reaction was carried out in the presence of chiral azacrown ethers and Lewis acid too, and we found that the enantiomeric excess decreased to 10-18%.

In the following experiments (R, R)-TADDOLs ($\alpha,\alpha,\alpha',\alpha'$-TetraAryl-1,3-Dioxolane-4,5-DimethanOLs) as chiral chelating diols were used. This family of compounds have been synthesized first by Seebach's group and used successfully as catalyst in various stereoselective syntheses [4]. As we found that the alkali metal complexes of TADDOL did not catalyse the phosphorylation reaction we decided to use its titan complexes as
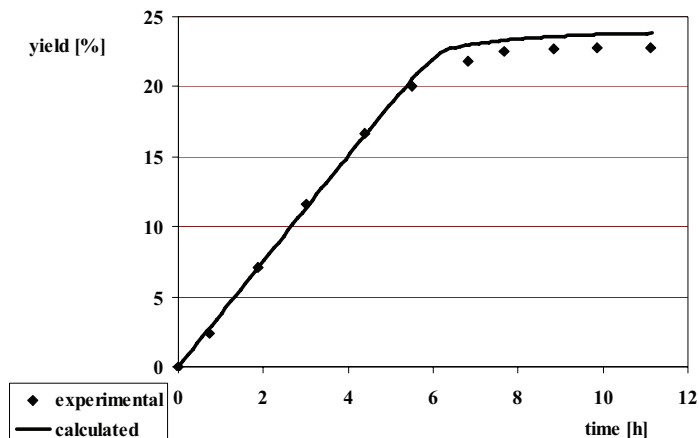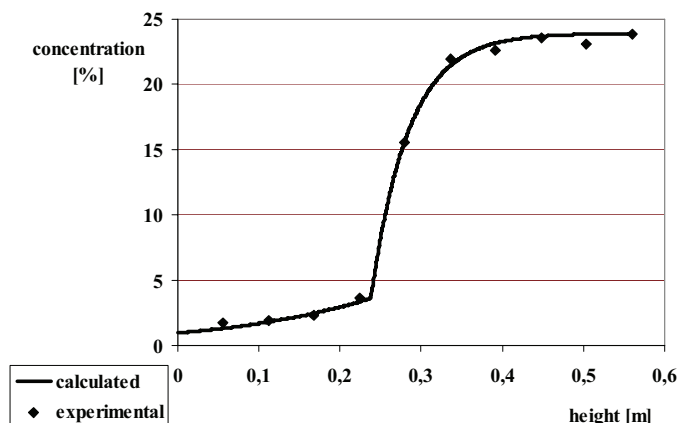
Fig. 29. The yield curve of the supercritical fluid extraction of once pressed corn germ in function of the time and the oil concentration in the solid matrix after a cut off experiment in function of the extractor height

chiral Lewis acid. Performing the reaction with diverse imines we found that the stereoselectivity is strongly influenced by the substituent (X, Y) of the aromatic ring of the imine, the chiral induction is very high (ee: 92%) in the case when X = nitro.

The *ee* values of the α-aminophosphonates have been determined by using chiral HPLC.

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Cyclotrimetallenes – Some Unsaturated Rings in the Carbon Group

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The first Group 14 cyclotrimetallene – cyclotrigermene – was synthesized in 1995 by Sekiguchi [1]. A few years later, the synthesis of cyclotrisilenes [2] the tin analogue [3] and the heteronuclear disilagermirene [4] were also reported. The physico-chemical properties and thermodynamic stabilities of cyclotrimetallenes have also been studied [5]. Among these interesting rings bicyclo compounds can also be found. Such a compound is tetrasilabicyclo[1.l.0]butane [6].

Unlike their carbon analogues, disilagermirene and tetrasilabicyclobutane have a tendency to undergo some unique isomerization. Detailed mechanisms of these reactions have been studied by means of computational chemistry. In this lecture the so far revealed mechanisms of isomerization reactions (Sch. 1, Sch. 2.) will be discussed.

Scheme 1.

white = hydrogen
tan = sylicon
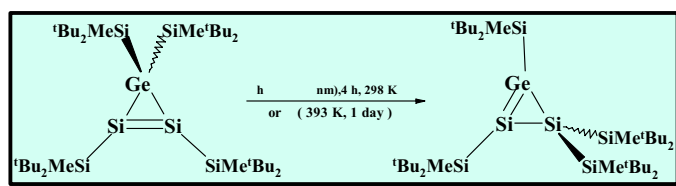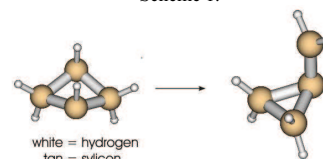
Scheme 2.

Fig. 31.

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Functional Studies of wheat Storage Proteins in a Model System

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The structure and composition of storage proteins in wheat and rice, the two most important cereals for human consumption, are extremely different. While the rice proteins are mostly globulins, the major seed storage protein in wheat are prolamins, capable to form gluten by their hydration providing unique rheological properties for the wheat-based products [1]. The inves-

tigation of model systems containing both rice and wheat components can lead to both theoretically and practically important observations.

Most of the knowledge about the functional properties of gluten proteins is derived either from indirect correlative studies, or from direct reconstitutive experiments [2]. In the first case, a number of samples with different chemical compositions and functions are characterized and then compared to each other using statistical methods. In case of reconstitution method the chemical composition of a base flour is altered systematically to study the effects. One of the limitations of the 'base flour' method is that the supplemented constituents obviously interact with the components of the flour. An ideal solution to avoid this problem would be to use base flour, such as rice flour, not containing any wheat flour components.
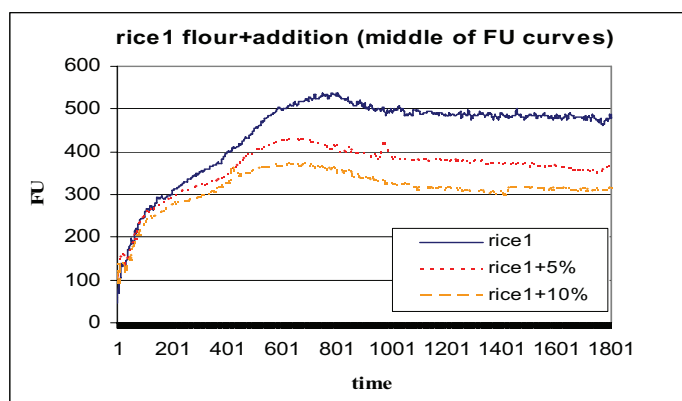

Fig. 32. Middle of the faringram curve of basic rice flour and with supplemented gluten

In this study the application of rice flour as a model system has been developed for the investigation of the functional properties of wheat gluten proteins with the particular aim to increase the elasticity of rice flour by the supplementation of wheat gluten. A faringraph was used to evaluate the impact of gluten addition on rice dough rheology. Various amounts of gluten were added *in vitro* into the rice flour. The height of the middle of the faringram curve is called consistency and is expressed in instrument related faringraph units (FU). Addition of wheat gluten changed the water absorption (WA), the maximum consistency (FU), the dough development time (DDT) and the mixing tolerance index of rice dough.

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Fluorescence Decay Dynamics of Indoline, N-methyl-indoline, Cyano-indoline and N-methyl-5-cyanoindoline in Solution

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N-methyl-5-cyanoindoline is used as a reference compound in several studies on the dual fluorescence of dimethylamino-benzonitrile (DMABN) [1].
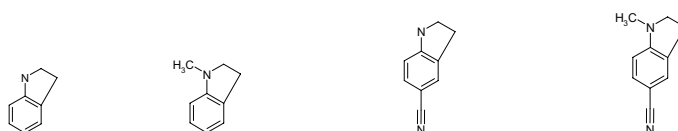

Fig. 33. The investigated molecules (indoline, N-methyl-indoline, cyano-indoline, N-methyl-cyano-indoline).
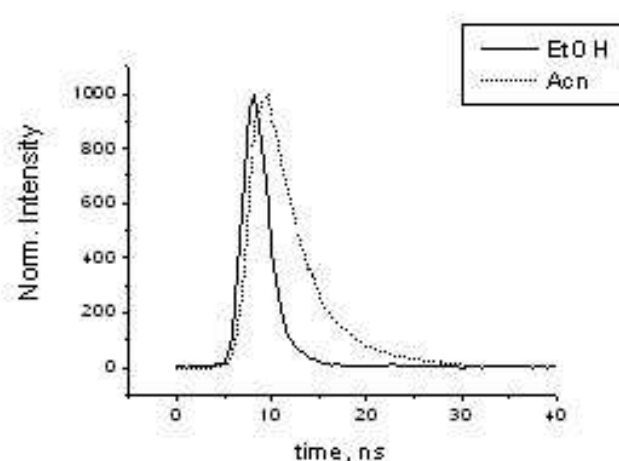

Fig. 34. The fluorescence decay curve of NMCI in acetonitrile and ethanol (the curves are obtained by TCSPC).

In the present investigation an attempt was made to make a comparative study on the photophysical behavior of indoline (I), N-methyl-indoline (NMI), cyano-indoline (CI) and N-methyl-5-cyanoindoline (NMCI) (see Fig. 33) in various solvents and solvent-mixtures at ambient temperature, in order to explore the deactivation processes that takes place for N-methyl-5-cyanoindoline. Despite of the structural similarities, these molecules differ to a large extent in their spectroscopic and photophysical properties. We have obtained the fluorescence quantum yields [2], the ISC (intersystem crossing) quantum yields and the fluorescence lifetimes of these compounds in order to understand the role of the substituents and also to elucidate the relaxation pathways. The used techniques were UV-VIS spectroscopy, fluorescence spectroscopy, TCSPC (time-correlated single photon counting) and flash photolysis [3]. It was found that the fluorescence lifetime of NMCI is substantially reduced in the presence of water and alcohol molecules. The reason for

the quenching in water for non-cyanated molecules is the electron transfer from the molecule to a cluster of water molecules [4]. In case of the cyano-substituted molecules an additional quenching effect takes place mediated by alcohol molecules. According to the obtained data in alcoholic solvents IC (internal conversion) is the dominant deactivation process.

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Study of phenylalanine ammonia-lyase by computational methods

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Besides the post-translationally cyclizing catalytic Ala-Ser-Gly triade, Tyr110 and its equivalents are the most conserved residues in the active site of phenylalanine ammonia-lyase (PAL), histidine ammonia-lyase (HAL) and other related enzymes. Molecular dynamics studies indicated that the Tyr110 "loop-in" conformation is more rigid without the C-terminal multihelix domain. On this basis it is hypothesized, that a role of this C-terminal extension is to decrease the life time of eukaryotic PAL by destabilization which might be important for the rapid responses in regulation of the phenylpropanoid biosynthesis.
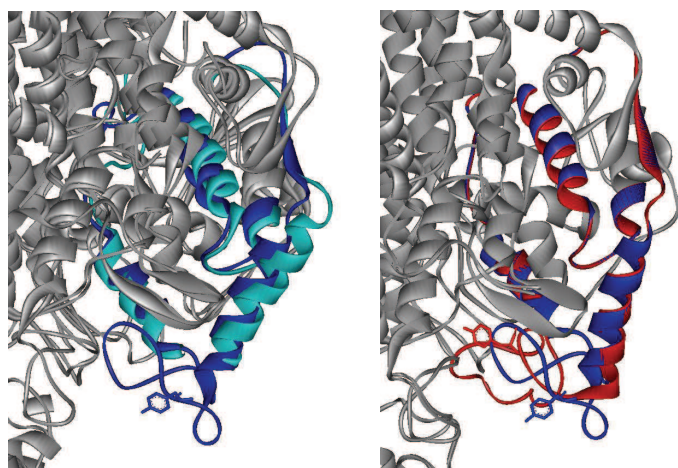

Fig. 35.

The structural and sequence similarity to HAL allowed the parsley (*Petroselinum crispum*) PAL, *Pc*-PAL structure to be constructed by homology modelling and to identify the catalytically important amino-acids [1]. This model resembles very much to the later appeared *Pc*-PAL crystal structure [3]. Kinetic

measurements show that Tyr110 is essential for the catalytic activity [1].

After resolving the crystal structure of one of the most studied fungal PAL, *Rhodotorula glutinis* (*Rhodosporidium toruloides*) PAL, (*Rt*-PAL) , a higher resolution *Pc*-PAL X-ray structure appeared [3]. An overlay of these two PAL crystal structures can be seen on Fig. 1. We coloured the incomplete Tyr110 loop region of *Rt*-PAL (cyan) and the complete but inactive Tyr110 loop in *Pc*-PAL (blue). In Fig. 2 the experimental *Pc*-PAL (blue) and our modified *Pc*-PAL structure with catalytically active Tyr110 loop (red) are depicted. The active Tyr110 "loop-in" *Pc*-PAL has lower energy than the "loop-out" conformation present in the crystal structure. We assumed this loop-out conformation to be catalytically inactive which is in accordance with the thermal inactivation of PAL enzymes. The presence of the inactive Tyr110 loop conformation may result in different isoforms of PAL enzymes, which could indicate negative cooperativity.

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Multiscale structure of PP/Montmorillonite nanocomposites

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The structure of a large number of layered silicate polypropylene nanocomposites were studied in a wide composition range. The silicate content of the composites was changed between 0 and 3 vol% and maleinated PP was added in 0-60 vol% to improve intercalation and/or exfoliation. Morphology characterization at different length scales was achieved by scanning and transmission electron microscopy, as well as by X-ray diffraction. The results showed that these materials possess a very complex structural architecture. The introduction of functionalized polymer decreased the size of the original clay particles and improved their interaction with the polymer matrix. However, relatively large silicate particles were also found in XRD images of composite samples without any silicate reflection. XRD supplies limited information if the amount of silicate is low, the

Fig. 36. Interaction of silicate layers at small clay (0.5 vol%) and large MAPP content (60 vol%); possible network formation of silicate sheets [1].

gallery distance of the stacks is large or their regularity is limited. On the other hand, XRD indicates intercalation. Although exfoliated individual layers can be detected by TEM, the method cannot be used to draw general conclusions about the structure of layered silicate nanocomposites because of statistical sampling and bias. A large number of individual layers, *i.e.* large extent of exfoliation, can lead to the formation of a silicate network structure, which can be detected by Cole-Cole plots of dynamic viscosity. We found that all four morphological entities (particles, intercalated stacks, individual layers, network) may be present simultaneously, *i.e.* the structure of the investigated PP nanocomposites is much more complex than usually claimed. The presence and relative amount of the different structural features definitely influence composite properties. However, currently used experimental protocols do not supply sufficient information even to estimate the relative influence and interplay among different structural features quantitatively. We may conclude, however, that XRD and TEM alone are not sufficient for the characterization of nanocomposites with complex structure.

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Analysis of the Debonding Process in Polypropylene Model Composites

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Particulate filled polymers are used in large quantities in many fields. The properties of these materials, just like those of all other heterogeneous polymers, depend on four factors: charac-

teristics of the components, composition, structure and interfacial interactions. Under the effect of external load, stress concentration develops around the particles and the actual stress distribution determines the local micromechanical deformation processes. In particulate filled polymers the dominating deformation mechanism is the separation of the matrix/filler interface, *i.e.* debonding. The extent of stress necessary to initiate debonding depends on the same factors mentioned above. In heterogeneous polymer systems the dominating micromechanical deformation process determines the macroscopic properties of the composite [1].
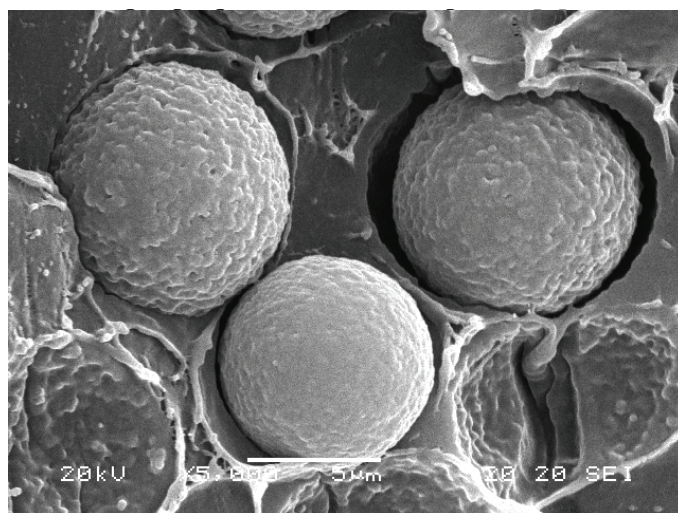

Fig. 37. SEM micrograph of cross-linked PMMA particles

The goal of the present research was to produce model composites from polypropylene (PP) and cross-linked PMMA particles of uniform size in order to obtain a better insight into the debonding process. The behaviour of the model composites were compared to that of $PP/CaCO_3$ composites containing commercial filler with a broad particle size distribution. An attempt was made to locate the initiation of debonding during deformation with acoustic emission (AE) experiments. The analysis of the AE signals gave valuable information about parameters influencing the debonding process, opened up possibilities for further studies, and for the eventual control of the process [2].

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Synthesis of 6-membered P-heterocycles with Exocicllic P-function in Position 3

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Our aim was to synthesize 1,2,3,6-tetrahydrophosphinine oxides with exocyclic P-function in position 3. The new heterocycles are of interest due to their potential bioactivity, and/or as precursors of P-ligands.

We wished to synthesize the target molecules by the Michael-type addition of diphenylphosphine oxide or dialkyl phosphites onto the electron-poor α,β-double-bond of 1,2-dihydrophosphinine oxides. Out of the possible 3-substituted tetrahydrophosphinine oxides only one of the diastereomers were formed [1].

Catalytic hydrogenation of the 3-diphenylphosphono- and 3-dialkylphosphono-1,2,3,6-tetrahydrophosphinine oxides gave the corresponding 1,2,3,4,5,6-hexahydrophosphinine oxides [2].
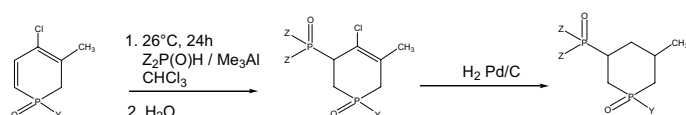
Y= Ph, *p*MePh, Et, EtO

Z= Ph, PhCH₂O, MeO, EtO

Fig. 38.

Conformations of the tetra- and hexahydrophosphinine oxides were evaluated [1, 2].

Complexation reactions of the corresponding bisphosphines with dichlordibenzonitrile platinum were also studied [3].

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Conversion of cycloaliphatic compounds on alumina supported Ir catalyst

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Nowadays, only a few percent of petroleum fractions is used in original, non-transformed form as fuels. The steadily growing output of engines requires the production of high quality fuels, gasolines with high octane number and gas oils with high cetane number.

In gasoline production the high octane number is achieved by using reformate gasoline rich in aromatic compounds, and/or alkylate rich in isoparaffins.

The aromatic compounds are more or less toxic because of their carcinogenic effect. The environmental protection forces the producers to replace aromatic compounds with other high octane number materials, like isoparaffines and ethers through the rules getting always stricter. These compounds are harmless in comparison with the aromatics. The so-called straight-run gasolines contain naphtenic compounds in a significant amount, those, which have longer side-chains should be converted into isoparaffins. The octane number increase is larger with longer side-chains.

The EXXON Research and Engineering Company conducted investigations, the results are patented, but proved that such conversion is possible and can be of economic advantage. (Int. Appl. Nr. PCT/US 96/14282, PCT/US96/14284). The main component of the catalyst was Ir beside other alloying metals, the supports were silica, alumina and zincoxide.

On the basis of these results we started our examinations in a laboratory reactor built by the experts of MOL Company.

The main part of this apparatus is the high pressure tubular reactor heated by a three-zone furnace. The hydrogen stream and the reactor pressure are automatically regulated. The experiments were carried out with a 1% Ir on alumina catalysts which was prepared in our laboratory with the impregnation of commercial alumina with $IrCl_3$ solution. The catalyst was reduced and activated in the reactor in hydrogen stream at 500^oC. The test material was methyl cyclohexane, the reaction temperature was $200\text{-}250^oC$ (because above 250^oC there was no fluid product), the liquid feed rate was $0,1\text{-}0,2$ cm^3/min. Measurable conversion was at $240\text{-}250^oC$ and at $0,1$ cm^3/min liquid feed rate with 5 g catalyst (Tab. 3).

According to these results the methyl cyclohexane was cleaved primarily at the secondary carbons affording 2- and 3-methyl hexane in more than 30%. The amount of 3-methyl hexane is the most that means the C-C bond being more distant from the tertiary carbon was cleaved preferentially. 2- and 3-methyl pentanes were also arisen in 4-10%, which presumes the simultaneous cleavage of two C-C bonds in the same molecule with the exit of methane.

Afterward we repeated these experiments at the same temperatures ($200\text{-}250^oC$) and we discovered that, the catalyst active temperature range was shifted. At 250^oC there was no considerable isoparaffin in the product. At higher temperature the product contained incremental amount of isoparaffins. We would like to analyse this range shift.

In summary, it is worth to carry on further research with Ir catalyst, after optimization of the reaction conditions, further substrates, support materials or alloying components can be investigated.

Raman Microspectroscopic Applications for Pharmaceutical Technology

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The significance of Raman microscopy is increasing in the field of pharmaceutical technology because of the very good lateral resolution, simple sample preparation and efficiency.

Tab. 3.

entry Nr.	Reaction conditions			Main products						
	Temp. ^{o}C	Liquid feed rate, cm^3/min	H$_2$ ml/min	2Me-pent %	3Me-pent %	2Me-hex %	3Me-hex %	3Et-pent %	n-heptane %	Me-chex %
5	240	0.1	60	2.1	1.8	10.1	18.8	0.2	0.7	65.9
8	240	0.15	90	1.5	1.3	7.4	13.6	0.1	0.5	75.2
9	250	0.1	60	4.8	3.7	16.4	29.1	0.6	1.3	42.4

The polymorphism of the active ingredient plays important role in the bioavailability, physical properties, and also in patents. The detection limit of the active pharmaceutical ingredient (API) is around 5% with NIR and XRD, because of the signs of inactive ingredients (IPI), but in case of pharmaceuticals with lower API content the only available technique for determining the polymorph forms is the Raman micro-spectroscopy. Its main advantage is the very small sample area ($d = 1\mu$m), where usually not all but some ingredients are present, thus the relative ratio of the component in question can be higher compared to the whole composition. This way the component can be characterized in low quantity, the polymorphic form is determinable [1] not just qualitatively but quantitatively [2]. The sensitivity is dependent on the Raman activity of the molecule, that is usually higher in case of APIs because they generally consist C=C double bond, aromatic ring or carbonyl group that can be polarized easily, and their vibration frequencies do not overlap with the bands of IPI's as it can be seen on Fig. 39.
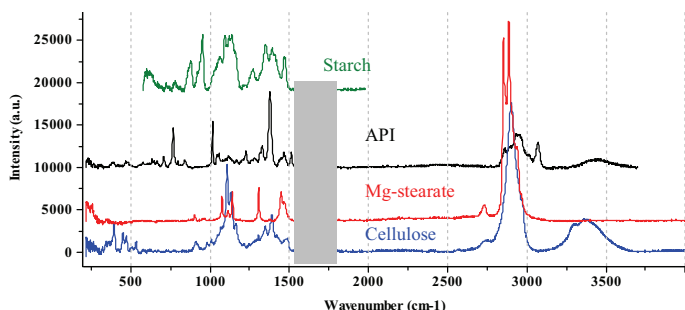

Fig. 39. Raman spectra of the IPI's and API

The Raman microspectroscopy makes it possible to characterize the interactions between the ingredients, thus the process of formulation can be developed by accessing molecular level information.

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Preparation of Hexagonal WO$_3$ by Thermal Oxidation of Hexagonal Ammonium Tungsten Bronze

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Tungsten oxides and oxide bronzes have attracted much attention in the past decades due to their possible chromogenic (electro-, thermo- and photochromic), sensory, catalytic and fuel cell electrode applications. One of the most studied tungsten oxides is hexagonal (H-) WO$_3$, since alkaline ions can easily get into their hexagonal channels under appropriate circumstances [1, 2]. H-WO$_3$ was synthesized first in the 80s by soft chemical methods [3]. It was mentioned elsewhere that H-WO$_3$ can also be produced by oxidation of hexagonal ammonium tungsten bronze, (NH$_4$)$_x$WO$_{3-y}$, HATB [4].

Recently, we investigated the formation of HATB by thermal oxidation and reduction of ammonium paratungstate, (NH$_4$)$_{10}$[H$_2$W$_{12}$O$_{42}$]·4H$_2$O, APT, and we proposed a model on its formation mechanism [5-7]. Our HATB sample obtained was more crystalline than the ones in the literature. Thus, it seemed advisable to explore what kind of H-WO$_3$ can be produced from our HATB sample.

We followed the formation of H-WO$_3$ through the thermal oxidation of HATB by evolved gas analysis (*on-line* TG/DTA-MS) and X-ray powder diffraction (XRD).

H-WO$_3$ was formed between 400 ˚C and 500 ˚C. The produced H-WO$_3$ sample was more crystalline than the ones prepared by soft chemical methods in the literature, and this may provide a possibility to investigate the characteristics and reactions of this compound in a more detailed way. Between 500 ˚C and 550 ˚C an earlier not observed exothermic DTA peak was detected, which was assigned to the hexagonal-monoclinic WO$_3$ transformation on the basis of XRD measurements. Between 700 ˚C and 750 ˚C another previously not described endothermic DTA peak was observed, which turned out to be reversible according to further DTA and XRD measurements, and might belong to the monoclinic-tetragonal WO$_3$ transformation (Fig. 40).
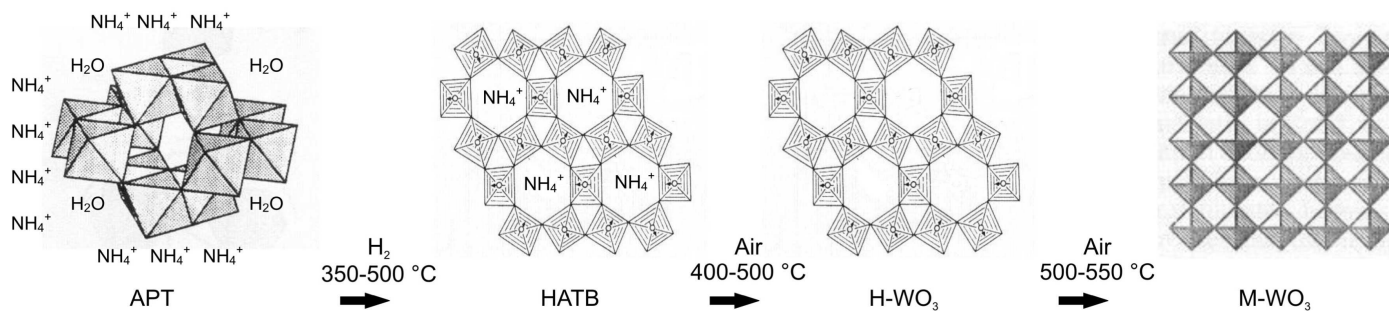
Fig. 40.

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A novel diagonal 2D gel electrophoresis technique for the identification of intrinsically unstructured proteins (IUPs) [1]

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According to the classical structure–function paradigm, proteins require a well-defined 3D structure to accomplish their functions. Nowadays a lot of proteins, that have special functions, turned out to be partly or fully disordered (IUP). This unusual structural property of numerous proteins was discovered by NMR examinations and was confirmed by other physicochemical techniques (CD-spectroscopy, gel filtration, DSC, SAXS etc.) as well. IUPs can play important roles in regulation, signal transduction or transcription such as $p21^{Cip1}/p27^{Kip1}$, α-synuclein (NACP), MAP2/tau, calpastatin, the N-terminal domain of prion protein. According to quantitative estimate, 10-20 % of various proteomes are unstructured, but only a handful of them have so far been identified.

The structure-function paradigm raised many new questions in connection with the function of IUPs. Thus, it is necessary to identify and study more IUPs, to develop a new method that provides data for extending the structure-function paradigm and to make it more complete and acceptable.
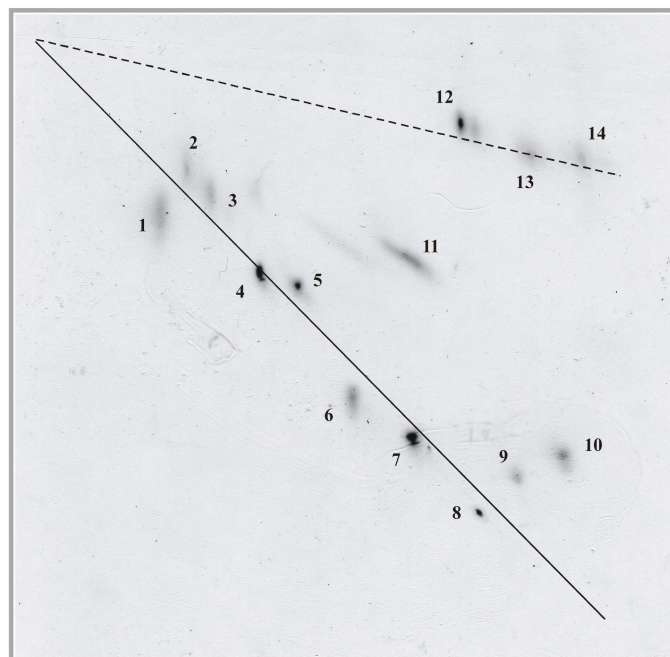

Fig. 41. IUPs: (1) stathmin **(2)** MAP2c, **(3)** MYPT1 304-511, **(4)** ERD10, **(5)** β-cazein, **(6)** α-synuclein, **(7)** CSTD1, **(8)** Bob1, **(9)** DARPP32, **(10)** α-cazein. **Globular proteins: (11)** serum fetuin, **(12)** IPMDH, **(13)** BSA, **(14)** ovalbumin.

In my paper I present a novel diagonal 2D gel electrophoresis technique. This technique takes advantage of the heat-stability of IUPs and their resistance to 8M urea. The principle and applicability of this method is shown on the following control gel.

In addition, I show some proteins identified by a combination of 2D gel electrophoresis with MALDI-TOF Mass-spectroscopy. Their structural speciality was investigated using prediction methods (PONDR, DISOPRED) and other structural studies (CD-spectroscopy, NMR, gel filtration).

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Flame Retardancy of Epoxy Resins with Reactive Additives and Nanoparticles

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According to the latest legislation of European Union the most widely used flame retardant additives in the epoxy resins, the bromine containing additives are banned from July 2006, [1] so their replacement *e.g.* by organophosphorous flame retardants became crucial. Many organophosphorous additives have low molecular mass which leads to the possibility of their loss from the polymer during high temperature processing or in the early phases of burning. Clearly, there was a need to increase the permanence of the additive within the polymer by incorporation of the organophosphorus functionality within the polymeric structure [2].

A simple and cost-effective method was developed in order to intro duce phosphorus moiety into the commercially available crosslinking agents for epoxy resins. This way phosphorus containing amine was synthesized (TEDAP), which functions both as crosslinking agent and flame retardant.

According to the thermal behaviour of the synthesized compounds, it can be concluded, that their decomposition is endothermic, what is advantageous in the aspect of flame retardancy, just as the significant charring. Their further enormous advantage over the traditional additives is that they do not increase the viscosity of the epoxy resin.

Tab. 4. Results of the Glow Wire Flammability Tests

Sample	GWFI value
AH-16 T-58 reference	550˚C
AH-16 T-58 20% TEDAP	550˚C
AH-16 T-58 40% TEDAP	650˚C
AH-16 T-58 60% TEDAP	750˚C
AH-16 T-58 80% TEDAP	850˚C
AH-16 100% TEDAP	960˚C

The synthesized phosphorus containing amine was incorporated into epoxy resin. The enthalpy of the curing followed by DSC confirmed that they can replace the traditional curing agents. Furthermore they perform an excellent flame retardant effect evaluated by LOI, UL-94, Cone Calorimeter and Glow Wire Flammability measurements. The best results were achieved in case of AH-16 100% TEDAP sample: the Oxygen Index of the epoxy resin sample could be increased from 21 to 33, and it achieved the best, V-0 classification according to UL-94 standard; the peak of the heat release rate was decreased to the fifth of the original value. Further improvement was measured by adding nanoparticles: In case of Fe MMT the LOI was increased to 36. It could be observed that the nanoparticles alone do not provide sufficient flame retardancy, but show significant synergic effect with phosphorus-containing flame retardants. During the Glow Wire Flammability Tests the best, 960˚C GWFI value could be achieved applying 100% TEDAP (*Table 4*), what means that the epoxy resin flame retarded this way is suitable for all kinds of electronic applications. The use of the epoxy resin flame retarded by this reactive additive could contribute to the development of safer computers and electronic equipment.

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Modelling Length Regulation of Stereocilia

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Stereocilia are cellular protrusions found on the surface of hair cells in the inner ear. They are essential receptors of hearing.

Stereocilia are composed of actin filaments crosslinked by the proteins espin and fimbrin. Although stereocilia persist for a lifetime, they undergo continuous renewal via molecular treadmilling: Monomers are incorporated at the tip (plus end) of the stereocilia and progress down toward the base. Filaments are depolymerized at the pointed (minus) end [1].

Stereocilia are organized into bundles with rows of different heights, forming a staircase pattern. The length of stereocilia within a row is constant and precisely maintained [2]. To achieve the balance, polymerization and depolymerization rates must be equal. What are the underlying molecular mechanisms of this balance? To answer this and related questions a mathematical model of stereociliar length regulation was developed based on the laws of reaction kinetics. In this lecture some conclusions deduced from our model will be presented.

References

1 **Rzadzinska AK, Schneider ME, Davies C, Riordan GP, Kachar B**, J. Cell Biol. **164** (2004), 887–897.

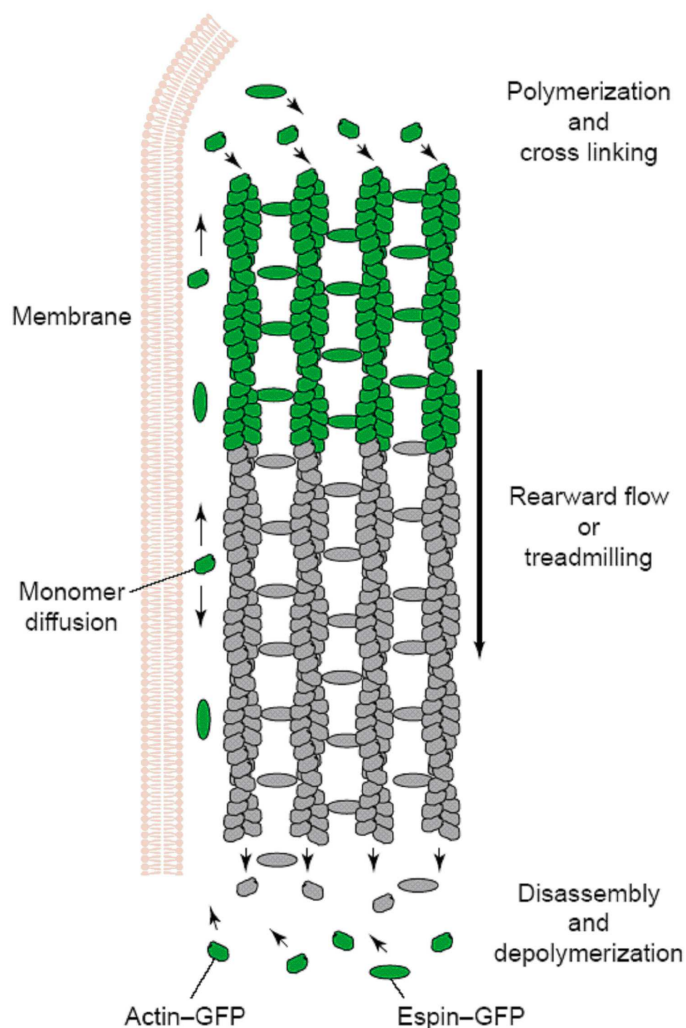2 **Lin HW, Schneider ME, Kachar B**, Curr. Op. Cell Biol. **17** (2005), 55–61.

Top right chemical structures with labels:

R= β-CH₂¹⁹-CH₃¹⁸ Ψ-vincadifformine (1)
R= α-CH₂¹⁹-CH₃¹⁸ 20-Epi-Ψ-vincadifformine (2)

R¹= α-H, R²=H Deethylibophyllidine (3)
R¹= β-H, R²=H 14-Epideethylibophyllidine (4)
R¹=H, R²= β-CH¹⁹(OH)-CH₃¹⁸ 19-Hydroxy-ibophyllidine (5)
R¹=H, R²= α-CH¹⁹(OH)-CH₃¹⁸ 19-Hydroxy-20-epiibophyllidine (6)

target compounds have been built up easily. According to our synthetic plan, the modification of substrates and the appropriately designed reaction partners provide opportunities for preparation of other, more complex frameworks of these alkaloids.

References

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The base-catalyzed, low-temperature interesterification of triglicerols: a new mechanism

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A number of mechanisms have been proposed in the literature for the base-catalysed interesterification reaction carried out at low ($<100°C$) temperatures. As these mechanisms are not in accordance with experimental observations, a novel mechanism will be proposed instead.

This novel mechanism assumes that the reaction of a base (such as sodium methanolate) with the oil will eventually lead to the abstraction of an α-hydrogen from a fatty acid moiety and that the enolate anion thus formed acts as the catalytic intermediate. This enolate can re-abstract a proton from the hydroxyl group of a partial glyceride whereupon the resulting alcoholate attacks the carbonyl group (Fig. 43). This leads to a new ester and a glycerolate anion and then the latter regenerates a new enolate anion. If the enolate anion reacts with methanol, this will lead to the formation of a fatty acid methylester and a glycerolate anion that again regenerates an enolate anion.

Reaction with water leads to catalyst inactivation by converting the enolate anion to an unreactive fatty acid moiety (free fatty acid or soap) and a partial glyceride.

Thermal inactivation of the enolate intermediate is assumed to be through the formation of catalytically inactive β-keto esters. The accelerating role of acetone is explained by assuming this compound to act as a highly mobile hydrogen transfer agent that facilitates the reaction between the glycerolate anion and α-hydrogen atoms in fatty acid moieties.

The above assumptions are independently supported by the observation that the addition of acetone-d₆ to an interesterifying

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Biomimetic synthesis of Aspidosperma and related indole alkaloids, together with their analogues. An efficient convergent synthetic pathway to build up the Ibophyllidine skeleton.
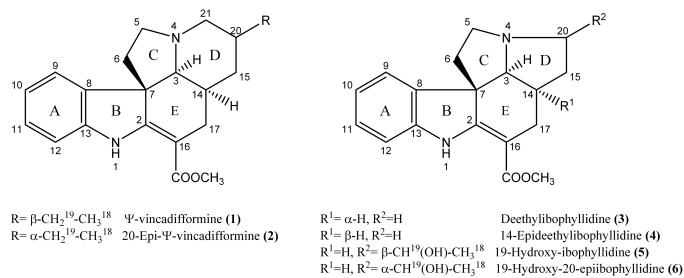
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The skeleton of indole alkaloids is represented in a great variety. The *Ibophyllidine* alkaloids are a type of pentacyclic monoterpenoid indole alkaloids belonging to the pseudoaspidosperma biogenetic class. These alkaloids have a skeleton with lack of the C 21 carbon, for this reason the six-member ring becomes five-member (D (21)-norpseudoaspidosperma skeleton) [1, 2].

In contrast to the widespread of research of *Aspidosperma* and *Strychnos* alkaloids, far less attention has been given to *Ibophyllidine* alkaloids. Accordingly, in our work we designed a simple synthetic route for pentacycles. In our convergent synthetic approach we intend to apply aldehydes as reaction partner to the N_b-benzyltryptamine derivative [3], whereby the
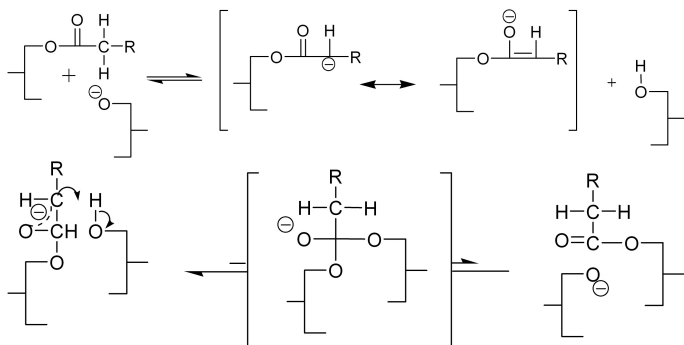
Fig. 43. Formation of the enolate anion; and its reaction with a partial glyceride

reaction mixture leads to the almost quantitative incorporation of deuterium into the α-position of fatty acid moieties. Theoretical calculations on the enolate - alcohol system at PM3 level are also in agreement with the enolate mechanism.

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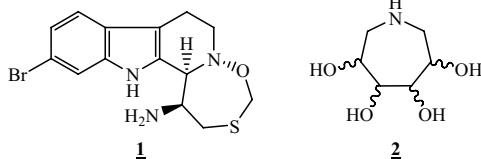
Synthesis of condensed-ring iminocyclitols from monosaccharide derivatives with Pictet- Spengler reaction

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The tetracyclic *eudistomin* alkaloids have unique structure (e.g.: *eudistomin K*, **1**) and show antiviral activity [1]. The *iminocyclitols* with seven member rings (**2**) and their derivatives also have antiviral activity [2].

Previously, we studied the *Pictet-Spengler* reaction of biogene amines and amino acid derivatives with aldehyde function to produce eudistomin alkaloid analogues. It was obvious from the literature that the condensed-ring *iminocyclitol* derivatives (e.g.: **3**) are worth to be built from monosaccharides, because the resulting compounds may also have antiviral effect. The keysteps of our planned synthesis gave some unexpected compounds, too (**4**, **5**).

R   = 2-(3,4-dimethoxyphenyl)ethyl-
Ac = COCH₃
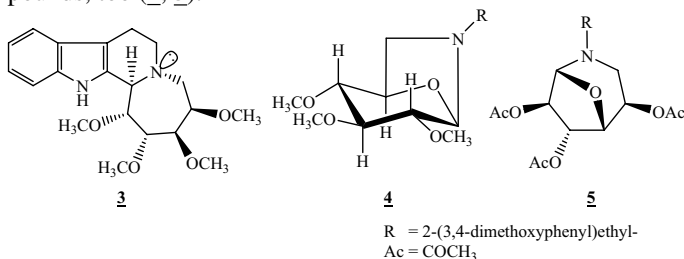
References

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## Synthesis of New Atropisomeric Compounds via Site Selective Metalation Reactions of 1-arylpyrroles

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The first members of rotationally restricted 1-arylpyrrole derivatives having C_1 symmetry were prepared by our research group five years ago [1]. Among these substances, 1-[2-carboxy-6-(trifluoromethyl)-phenyl]pyrrole-2 carboxylic acid was also applied as chiral ligand. Recently, we examined the synthesis of 1-(substituted phenyl)pyrroles having significant rotation hindrance around the C-N bond. These compounds can be separated into their enantiomers and can be used as chiral ligands, as well. We investigated mono- and dimetalation of compounds **1-4** with various activated organometallic or alkali amide type bases. Highly regioselective lithiations were accomplished with appropriorate selection of the reaction conditions (ligand, organometallic reagent, solvent, temperature, and reaction time). Thus, numerous new mono- and dicarboxylic acids were synthesized. In addition, we attempted the asymmetric substitution of the α and α' positions of the pyrrole ring with different substituents (**5-7**).
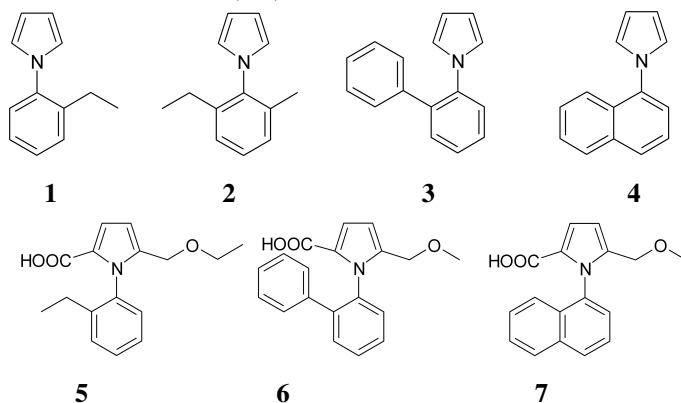
The rotationally stable dicarboxylic acid atropisomers were separated with optically active 1-phenyl-ethylamine.

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