NEWSLETTER

Editors: Svetlana Bratskaya, Institute of Chemistry FEBRAS, **Vladivostok**, Russia
E-mail s.bratskaya@gmail.com;
Martin G. Peter, University of **Potsdam**, Germany
E-mail Martin.Peter@uni-potsdam.de

August 2016
No. 37

Editorial

Dear EUCHIS Members,

In these summer days, we are pleased to present you a new issue of the EUCHIS Newsletter.

A critical review on abundance of chitin in the biosphere by Prof. Martin Peter in the Forum section invites you to get rid of stereotypes that "chitin is the second most abundant natural biopolymer" and admit that there is no sense in comparing the relative abundancies of polysaccharides. As usual, your comments are welcome! We gently remind you that, aside from Newsletter, we have a Forum platform in the EUCHIS website, which is not very active yet but we are all responsible for positive changes.

Anticipating the next EUCHIS conference, whose dates and venue are announced in the Message from President, we still receive feedbacks from 12th EUCHIS / 13th ICCC. In this issue, you will find the Travel grant report of one of the six grant awardees.

After the silence period, several national and international meetings on chitin and chitosan will be held in September, 2016 (p.10). You can still join some of them, if you have not done it already.

Enjoy the summer time, come back, and send us your contributions, suggestions, and comments to make the EUCHIS Newsletter and the web site more exciting and informative!

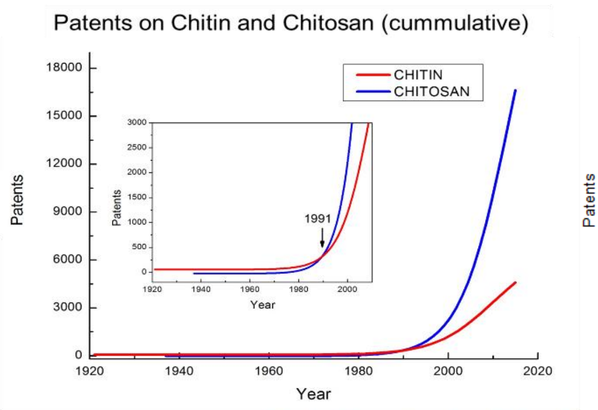
Svetlana Bratskaya, Secretary (s.bratskaya@gmail.com)
Martin G. Peter, Assistant Secretary (Martin.Peter@uni-potsdam.de)

Message from the President

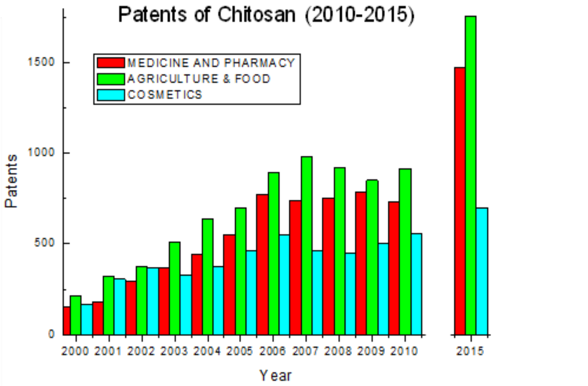
Silence, we are shooting!

2016 is being an intermediate year between the Münster EUCHIS meeting in 2015 and the next one in Seville at June 1st-4th 2017: "**13th International Conference of the European Chitin Society - VIII Simposio de la Sociedad Iberoamericana de la Quitina**".

Members of the Chitin-Chitosan family are using their time, to put it in Hesiod´s wording, their "works and days" just producing new knowledge and new applications: more than forty patents have been registered so far along this unfinished year and a similar number of publications in scientific journals. As for the patents, I enclose two tables from WIPO to support my optimistical point of view:



Source: WIPO: https://patentscope.wipo.int/search/en/search.jsf



Source: WIPO: https://patentscope.wipo.int/search/en/search.jsf

No matter the political turmoils around us, no matter the outcome of the *Brexit* referendum, no matter who has won the UEFA Euro 2016 or the Olympic Games, the Chitin family simply asks kindly but firmly "silence, we are shooting" , as in the film industry.

Let me remember an old dictum of Johann Joachim Becher, a seventeen century German chemist : *The chemists are a strange class of mortals, impelled by an almost insane impulse to seek their pleasures amid smoke and vapour, soot and flame, poisons and poverty; yet among all those evils I seem to live so sweetly that may I die if I were to change places with the Persian king.*

I am quite confident that none of us should change places with the Persian king either, should we?

Ángeles Heras

President of EUCHIS

Forum

On the abundance of chitin in the biosphere and its importance

It is often said that chitin

- is the second most abundant natural biopolymer[1];
- is the second most abundant natural biopolymer after cellulose[2-4];
- belongs to the most abundant natural polymers, after cellulose[5];
- is the second most abundant organic compound in nature, after cellulose[6];
- chitin is the second most abundant semi-crystalline polysaccharide[7].

This is repeated over and over again in journal publications, dissertations, and conference presentations. Correct: cellulose and chitin are one class of biopolymers, namely polysaccharides. Other classes of biopolymers are proteins, nucleic acids, and polyphenols. With few exceptions, a rationale for the estimates or references which would allow reasonable calculations of the amounts of chitin and cellulose and a ranking of their abundances are not cited. Thus, it is appropriate to look at some facts:

Chitin and cellulose have a variety of similar physicochemical properties on common, such as semi-crystallinity, insolubility in most solvents, polydispersity, and existence of polymorphs. Estimates for the annual production of chitin and also its steady state amounts in the biosphere vary between 10^{10} and 10^{11} tons. Similarly, estimates for the production of cellulose in plants vary by two orders of magnitude between 1.3×10^{10} and 1.5×10^{12} tons (Table 1). Taking the lower numbers, chitin would be nearly as abundant as cellulose. With the higher estimates, cellulose would be 15 times more abundant than chitin.

Table 1. Estimated annual biosynthesis of chitin and cellulose.

Polysaccharide	Biosynthesis (Billion = 10^9 Tons)	Equivalent in Organic Carbon (Billion Tons)[a)]	Ecosystem	References
Chitin	10 – 100	4.73 – 47.3	Global	[8,9]
	2.3	1.09	Marine waters	[10]
	1.362	0.64	Hydrosphere	[11]
Cellulose	13	5.77	Global	[12]
	> 100	44.45	Global	[13]
	1 500	666.8	Global	[14]
Starch	unknown			

a) Biomass is expressed in equivalents of organic carbon which also is used for biopolymers. The elemental composition of chitin is [$(C_8H_{13}NO_5)_n$; C = 47.29 %] and of cellulose or amylose is [$(C_6H_{10}O_5)_n$; C = 44.45%]. Lignin, calculated as a polymer of coniferylalcohol with only one C-C- or C-O-bond per unit, is [$(C_{10}H_{10}O_3)_n$; C = 67.41 %].

Secondary cell walls of all land plants are composed of more or less 30 - 50 % of cellulose, 20 - 50 % of hemicelluloses [principally xylans, (arabinoglucurono-)xylans, mannans, xyloglucans, glucomannans, and β-(1→3,1→4)-glucans)[15], and 20 – 30 % of lignin which all are biopolymers. Taking the higher numbers of estimated abundancies, other biopolymers in plants would be roughly as abundant as cellulose. Chitin would then rank in the fourth or fifth place behind hemicelluloses and lignin. In fact, some authors rank lignin as the second most abundant natural product after cellulose[16].

Starch is another very abundant mixture of amylose and amylopectin but estimates on its abundance are not available. Nevertheless, some authors believe that starch is the second most abundant carbohydrate in the biosphere after cellulose[17].

There are, however, some inconsistencies: Total plant biomass on earth is estimated to contain 833×10^9 tons of organic carbon[18]. When cellulose biosynthesis is expressed in equivalents of organic carbon (Table 1), then between 5.4 and 80.3 % of plant biomass would be cellulose. Both numbers are obviously far from reality.

Another item is usually not considered, namely the procaryotes (archae and bacteria) which according to Whitman et al.[19] contain $350 – 550 \times 10^9$ tons of organic carbon. Procaryotes do not produce chitin, but some bacteria synthesize modified chito-oligosaccharides as Nod-factors. The polysaccharides of bacteria are, in general, mureins and a large variety of highly diverse capsular polysaccharides. Some bacteria produce other polysaccharides like e.g. alginates, cellulose, gellan, hyaluronan, or xanthan, but the global abundancies of these biopolymers are unknown. In consequence, one may speculate that the most abundant biopolymers on earth are proteins and/or nucleic acids ? However, those are heteropolymers and may not be compared with the homopolymers cellulose, amylose, or chitin.

It is also said sometimes that chitin is the second most important natural polymer in the world[20]. The importance of a material is based on several factors: production, applications, and market value. One may also include the biological function, but – in my eyes – there is nothing unimportant in nature.

Given that cellulose, starch, and chitin are very abundant, production does not depend on the amounts produced in nature, but on accessibility of the raw material and on the demand which depends on its uses. The logistics of securing raw materials differ fundamentally: cellulose and starch are readily accessible from plantations where trees, corn and other crops are grown primarily for production of the raw materials, whereas chitin comes as a byproduct of seafood industry. Nobody would think about setting up a shrimp farm or a krill catching fleet for the sole purpose of chitin production.

The primary source for cellulose is wood which is used mostly for paper and board fabrication (Table 2). The global demand of the paper industry is currently ca. 400×10^6 tons of cellulose, about 60 % of this comes from recycled paper[20]. Minor amounts of cellulose are used for fibers and films. Cellulose-based textiles are primarily produced from cotton or from regenerate cellulose fibers. Flax, hemp, and jute play a minor role in this application.

Table 2. Production, main applications, and markets of cellulose, starch, and chitin.

	Industrial Production (Year) (10^6 Tons)	**Main Application**	**Price (USD per Ton)[b)]**
Chitin	< 0.1[a)]	Glucosamine (65%); Chitosan (25%); Chitooligosaccharides (10%)	Chitin 6000 – 40 000; Chitosan: 15 000 – 160 000[22]
Cellulose	160 (World; 2003)[14,21]	Paper and Board (98%) Derivatives, mainly regenerate fibers for textiles, Films, etc. (2 %)[14]	Wood Pulp: 875 Cotton: 1600[23]
Starch	10.5 (EU, 2014)[24,25] 66 (World, 2008)[26]	EU: Food (61%); Feed (1%); Non-Food (mainly paper additives; 38%)[25] US: Food (45%); Ethanol (40%)[26]	200 – 1300[27]

a) Production of chitin is probably not larger than 40 000 tons per annum. However, reliable figures are not available.

b) Prices vary widely, depending on the source of raw material, and the quality (purity) of the product. Original quotations, as taken from the cited web-sites, are in USD / Kg for chitin and chitosan, in USD / ton for wood pulp and starch, and in US cents per pound for cotton.

The annual global demand for starch is about 66×10^6 tons, most of which is used in the food industry as a viscosity modifier and for sweeteners in the form of glucose syrup. In the U.S., and in smaller amounts also in Europe, starch producing crops, mostly maize and potatoes, respectively, are also cultivated for ethanol production[24,25]. Additional data and many other applications can be found on the homepage of the International Starch Institute[26].

The primary source for chitin is waste from shellfish (krill, shrimps, crabs, lobsters) processing for food, with a currently global availability of the raw material of 6 – 8 million tons, containing roughly 15 – 40 % of chitin[4]. Estimates for the actual global industrial production of chitin are in the range $0.02 - 0.04 \times 10^6$ tons, most of which is used for manufacture of glucosamine.

It is also mentioned sometimes, that chitin may be used as a renewable resource for the production of bulk chemicals, like ethanolamine which is used in amounts of annually ca. 2×10^6 tons, and other nitrogen containing compounds[4]. Some suitable chemical processes were so far demonstrated on the lab scale. However, the limited accessibility of chitin and the processing cost leave little chances for those ideas.

Chitin, besides being the only known source for industrial production of glucosamine, is also converted to chitosan and to oligosaccharides. Chitosan, as a cationic polyelectrolyte, has many unique physicochemical and biological properties which render it a valuable component for materials and pharmaceuticals[28], not considering the debatable advertisements as a "fat blocker". The most promising applications of chitosan are probably in the fields of wound healing and drug delivery. Oligosaccharides are used in agriculture in some countries as growth regulators. Pharmaceutical applications of chito-oligosaccharides, e.g. for treatment of rheumatoid diseases, are expected to achieve registration in the near future. Of course, there are many other suggested applications, often reviewed in the literature, but only a few of them are put into practice.

In the last two decades, basic research on chitin, chitosan and the enzymology of these polysaccharides has yielded some fundamental results of general interest. Among those is the discovery of chitinases in humans and of the receptor-mediated function of chitosan, and also chito-oligosaccharides, as signal transmitters in certain bacteria, plants and animals, respectively. Another highly important discovery was the identification of a lytic polysaccharide monooxygenase (LPMO) in a bacterium[29]. This enzyme acts on crystalline chitin and facilitates its degradation by hydrolytic chitinases. Similar enzymes have been found which cleave cellulose, amylose, and xyloglucans, respectively, opening the way for a new technology of enzymatic saccharification of these polysaccharides and "second generation ethanol" fermentation of hitherto unused waste materials, such as bagasse and lignocellulose.

In summary, cellulose, starch, chitin, and many others are very abundant polysaccharides. However, there is no sense in comparing the relative abundancies of polysaccharides and other biopolymers, because this implies too many unknowns and is not of any practical relevance. Also, there is no sense in comparing their importance. Cellulose is mostly good for paper, starch is good for food, and chitin is good for glucosamine, for chitosan and for chitooligosaccharides. All the many other applications are minor in quantity, but are already or may be in the future very important, too.

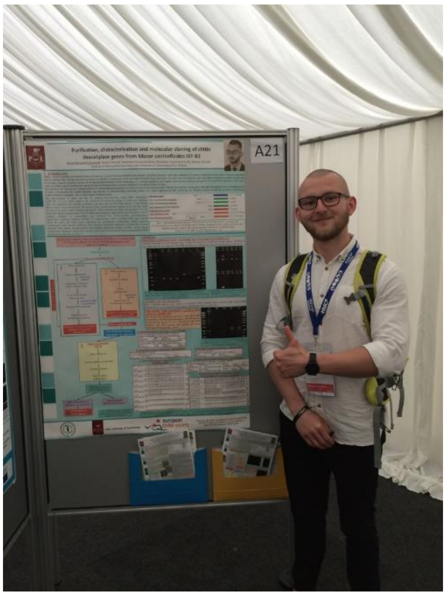
Of course, this essay is a reflection of my personal ideas and interests. Comments are very welcome and appreciated!

Martin G. Peter

References

1. Tharanathan, R. N.; Kittur, F. S., *Crit. Rev. Food Sci. Nutr.*, (2003) **43**, 61-87; http://dx.doi.org/10.1080/10408690390826455.
2. Shahidi, F.; Arachchi, J. K. V.; Jeon, Y.-J., *Trends Food Sci. Technol.*, (1999) **10**, 37-51.
3. Khan, F.; Ahmad, S. R., *Macromolecular Bioscience*, (2013) **13**, 395-421.
4. Yan, N.; Chen, X., *Nature*, (2015) **524**, 155-157; http://dx.doi.org/10.1038/524155a.
5. Younes, I.; Rinaudo, M., *Mar. Drugs*, (2015) **13**, 1133-1174; http://dx.doi.org/10.3390/md13031133.
6. Martínez, J. P.; Falomir, M. P.; Gozalbo, D., *eLS*, John Wiley & Sons: 2001; http://dx.doi.org/10.1002/9780470015902.a0000694.pub3.
7. Zeng, J. B.; He, Y. S.; Li, S. L.; Wang, Y. Z., *Biomacromolecules*, (2012) **13**, 1-11.
8. Gooday, G. W., *Adv. Microb. Ecol.*, (1990) **11**, 387-430; http://dx.doi.org/10.1007/978-1-4684-7612-5_10.
9. Gooday, G. W., *Biodegradation*, (1990) **1**, 177-190; http://dx.doi.org/10.1007/BF00058835.
10. Jeuniaux, C.; Voss-Foucart, M.-F.; Bussers, J.-C., *Aquat. Living Resour.*, (1993) **6**, 331-341; http://dx.doi.org/10.1051/alr:1993034.
11. Cauchie, H.-M., *Hydrobiologia*, (2002) **470**, 63-96.
12. Sandermann, W., *Holz Roh. Werkst.*, (1973) **31**, 11.
13. Brown, R. M., Jr., *J. Polym. Sci., Part A: Polym. Chem.*, (2004) **42**, 487-495; http://dx.doi.org/10.1002/pola.10877.
14. Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A., *Angew. Chem., Int. Ed.*, (2005) **44**, 3358-3393; http://dx.doi.org/10.1002/anie.200460587.
15. Scheller, H. V.; Ulvskov, P., *Annu. Rev. Plant Biol.*, (2010) **61**, 263-289; http://dx.doi.org/10.1146/annurev-arplant-042809-112315.
16. Daebeler, S.; Peters, D., *Gülzower Fachgespräche* (2009) **31**, 250-259; http://dx.doi.org/http://www.fnr-server.de/ftp/pdf/literatur/pdf_367-gf_band_31_lignin_100dpi.pdf.
17. Blennow, A.; Nielsen, T. H.; Baunsgaard, L.; Mikkelsen, R.; Engelsen, S. B., *Trends Plant Sci*, (2002) **7**, 445-450.
18. Sitzmann, H., *in: Römpp-Online*, (2006); http://dx.doi.org/https://roempp.thieme.de/roempp4.0/do/data/RD-11-01491.
19. Whitman, W. B.; Coleman, D. C.; Wiebe, W. J., *Proc. Natl. Acad. Sci. U. S. A.*, (1998) **95**, 6578-6583; http://dx.doi.org/10.1073/pnas.95.12.6578.
20. Rinaudo, M., *Prog. Polym. Sci.*, (2006) **31**, 603-632; http://dx.doi.org/10.1016/j.progpolymsci.2006.06.001.
21. Verband Deutscher Papierfabriken e.V., VDP-Statistiken, (2016); http://www.vdp-online.de/de/papierindustrie/statistik.html.
22. Alibaba Trading Group, https://www.alibaba.com/showroom/for-chitin-price.html, (2016).
23. Index Mundi, http://www.indexmundi.com/commodities/?commodity=wood-pulp, (2016).
24. VDGS e.V. (Verband der deutschen Getreideverarbeiter und Stärkehersteller e.V., http://www.staerkeverband.de/html/staerke.html, (2014).
25. European Starch Industry Association, Starch Europe, http://www.starch.eu/european-starch-industry/, (2014).
26. International Starch Institute A/S, (2014); http://www.starch.dk/ISI/market/index.asp.
27. International Starch Institute A/S, (2014); http://www.starch.dk/isi/market/market.asp.
28. Peter, M. G., *Advances in Chitin Science*, (2014) **14**, 339-346; http://www.euchis.org/wp-content/uploads/2015/04/proceedings_14.pdf.
29. Vaaje-Kolstad, G.; Westereng, B.; Horn, S. J.; Liu, Z. L.; Zhai, H.; Sorlie, M.; Eijsink, V. G. H., *Science*, (2010) **330**, 219-222. http://dx.doi.org/10.1126/science.1192231.

EUCHIS Travel Award



Michal Benedykt Kaczmarek
Lodz University of Technology, Poland

MSc Eng, born in 1990. He obtained a BSc degree in molecular biotechnology and technical biochemistry from Lodz University of Technology. In 2011, he also started another academic course at the same university – a BSc course in chemical technology – in the field of the technology of polymers.

His experience in biotechnology has grown in the course of the passing years, as he has participated in international internships at the University of Houston-Downtown (USA, 2013) and at the University of Groningen (Netherlands, 2014). During that period, he was able to focus both on experimental and theoretical matters related to diverse subjects.

He was able to apply his experience and skills in numerous R&D projects. He has actively participating in projects to study biotransformations for the pharmaceutical and cosmetic industry as well as the application of biomass for the production of environmentally friendly polymer materials. He was awarded an MSc degree in September 2014, after which he started a PhD course at the Faculty of Biotechnology and Food Sciences at Lodz University of Technology.

While searching for his scientific domain combining both areas, he has become interested in two astonishing biopolymers, namely chitin and its derivative, chitosan. As a matter of fact he had already worked with these fascinating and unique biopolymers during his MSc course, when he took part in research projects on enzymatic modification of chitin and isolation of chitin and chitosan from the cell wall of filamentous fungi *M. circinelloides*.

Moreover, he has been an active member of the Polish Chitin Society since 2013 and a member of the European Chitin Society since 2015 as well. Currently, at the first stage of scientific career as a PhD student, which started in October 2015, he intends to engage in the research on these biopolymers. He has commenced a research project aimed at an artificial chitinosome construction, i.e. a multi-enzyme complex which would enable the one-step selective and efficient modification of chitin and chitosan. His task now is to obtain preparations of chitinolytic and chitosanolytic enzymes from selected filamentous fungi. To accomplish this, he has detected and cloned two genes encoding chitin deacetylase. The current attempt is to find a eukaryotic protein expression system, which can be used for high-level and large scale production of recombinant proteins.

In November 2015, Michal Kaczmarek was awarded for his previous achievements by Lodz city authorities as the best PhD student.

EUCHIS Travel grant report

The 12th International Conference of the European Chitin Society and the 13th International Conference on Chitin and Chitosan held by the European Chitin Society are among the most valuable and promising events in my entire life. Therefore, I would like to express my sincere gratitude to all conference hosts, in particular Ms Angeles Heres, the EUCHIS president, who awarded me a travel grant. This financial support provided me with a unique opportunity to develop my knowledge of two incredible polymers, namely chitin and chitosan.

From my point of view, this event was perfectly arranged in every aspect. The campus of the University of Munster was the first to catch my attention and impress me, as it has an unparalleled atmosphere and is full of greenery. At first, as newly minted and inexperienced PhD student, I had some doubts whether I would be able to handle such an important and prestigious conference. However, the doubts immediately and entirely dispelled thanks to the staff in charge of registration of conference participants; the staff made me feel at home. They explained all the details and indicated the most important places. All this helped me to settle in a new situation. Moreover, the outstanding mobile app developed especially for this occasion is also worth mentioning. This app provides the most important information, such as a detailed conference programme, locations of restaurants, canteens and the most interesting places in Munster. Additionally, it enabled all participants to vote quickly and easily for the best posters and presentations. The app proved to be indispensable more than once.

As far as I am concerned, the most important elements of the conference, which caught my attention, included the lectures given by the greatest specialists involved in the research on chitin and its derivatives from all over the world. Since I have realised that I would like to engage fully in the work on chitin and chitosan, such a conference has been the fulfilment of my dreams. I am certain that an active participation in these lectures offered me a unique opportunity to develop my knowledge and find new ideas of how to proceed with my research. Additionally, it was a great chance to network with other professionals from the world, which was an exceptional opportunity for the exchange of experience.

Last but not least, I would like to mention the technical workshop arranged by the hosts, in which I had a great pleasure to participate. Lectures conducted by the researchers from the University of Munster, presented in a simple and fast manner, showed and explained modern techniques and methods applied in the research on chitin and chitosan. The experience and knowledge gained during the technical workshop has continued to provide positive results during my recent research.

To summarise, I cannot emphasise too much that this conference has been one of the greatest events in my entire professional live. I must admit that the people, who I met, as well as the experience and knowledge, which I gained during these three wonderful days, certainly developed my personality and gave me new ideas for my recent research. I look forward to attending the next edition of the conference held by the European Chitin Society.

Forthcoming Meetings

11th APCCS (Asian-Pacific Chitin-Chitosan Symposium)
28-30th September, 2016, India.
Dead line for Poster Presentations is 12th August, 2016!

XXII Conference of the Polish Chitin Society "New Aspects of the Chemistry and Applications of Chitin and its Derivatives"
14-16th September, 2016, Malbork, Poland

XIII International conference of the Russian Chitin Society «Modern Prospects in Chitin and Chitosan Research»
5-10th September, 2016, Ufa, Russia

13th EUCHIS / 8th SIAQ Conferences (European Chitin Society / Sociedad Iberoamericana de Quitina)
1st-4th June, Seville, Spain. Further updates are expected in September, 2016.

14th ICCC / 12th APCCS (International Chitin-Chitosan Conference / Asian-Pacific Chitin- Chitosan Symposium)
will take place jointly in 2018 in Osaka, Japan. Further information will be published in due course in the web.