

Short History of Cassia Gum

When the end of the 70ies had seen a year of exploding guar gum prices, a few dedicated chemists at the former Diamalt AG in Munich came across a potential substitute for guar gum in form of a seemingly rather exotic leguminose seed from India's cornucopia of valuable forest products.

It was understood to be a promising source for a guar surrogate, however, the polysaccharide from the endosperm of these strange leguminose seeds turned out to be a galactomannan with much different properties than the ones of the guar cluster bean.

Not common to the European flora, these exotic seeds had been taxed as *Cassia occidentalis* in the beginning, and after having discovered that after firm chemical functionalisation this new gum had excellent film forming properties, a patent was filed for the use of etherified *Cassia occidentalis* Gum as a sizing agent for cotton staple fibre yarns and even for polyester filament yarns.

Not long after, it became obvious that the seeds had been erroneously held for *Cassia occidentalis*, and the taxonomic assessment under the guidance of a German botanical professor led to the conclusion that the seeds should be allocated to the plant species *Cassia tora*, synonymous *Cassia obtusifolia*.

In the following, some new industrial applications for *Cassia tora* syn. *obtusifolia* had been developed, besides others as thickeners in printing pastes containing vat dyestuffs, acid dyes, disperse dyes, to be applied on various fabric substrates as rayon, cotton, polyester, even silk.

Also, carpet printing thickeners for metal complex dyestuffs had been marketed. Further industrial applications of *Cassia* derivatives involved slime depressants in ore and mineral beneficiations. Other uses had been water retention aids in paper coatings on light weight papers for rotogravure printing. Even cationic *Cassia* derivatives for improving the hand on fabrics for personal care and in hair conditioners had been tested commercially with success.

All this helped to commercialise the raw material *Cassia* galactomannan with special emphasis to the quality improvement of the seed endosperm sections, concerning cleanliness and absence of foreign matter.

However, the most prominent and striking property of *cassia* gum lies in the fine structure of its poly-galactomannan matrix, with its great similarity to locust bean gum, which leads to a unique synergism with κ -carrageenan, extracted from "*Kappaphycus alvarezii*" or

"Kappaphycus striatum", commonly known under their trade name cottonii (Eucheuma cottonii) when harvested under commercial algae farming conditions.

This prominent feature of synergistic interactions of cassia gum with κ -carrageenan and for example also with xanthan gum, led to another set of patents. By the end of the 80ies it became very clear, that again there was a need for a revision of the botanical classification of "our" Cassia Gum source.

After having realised the differences in the epidermal area of the seeds received from India, a selection and differentiation of the seeds was possible.

Two types of seeds could be sorted by optical selection means: The two fractions showed differences in the seed weights, amino acid profile of the seed germ, and especially in the profile of secondary metabolites resulting from the phytochemical acetyl-CoA / malonyl-CoA condensation pass way leading to aromatic polyketide structures.

From these findings, it was clear that Cassia tora and Cassia obtusifolia are two distinct species. Admittedly, Cassia L. sens. lat. belongs to the 25 largest genera of dicodyledonous plants in the world, and with more than 600 species occurring mostly in the tropics and subtropics, the taxonomy and nomenclature delimitating the species is not easy.¹

Dr. V. Singh has covered this topic in an outstanding publication "Monograph on Indian Subtribe Cassiinae (Caesalpiniaceae)".¹ Some taxa are very closely related in gross morphology, ecological requirement and even in the seed chemistry.

"The constant differences between them are few and relative minor, involving seed and anther morphology, seed weight, vegetative characters, and epidermal features", citing Dr. Barbara R. Randell.²

The pleurograms and the areoles of Senna tora and Senna obtusifolia are quite different from each other (© Glycomer GmbH):



By suggestion of Irwin & Barneby³ an improved classification raised the genus *Cassia* L. to the level of subtribe *Cassiinae*. This subtribe comprises three genera, namely *Cassia* L. sens. str., *Senna* P. Mill., and *Chamaecrista* Moench.

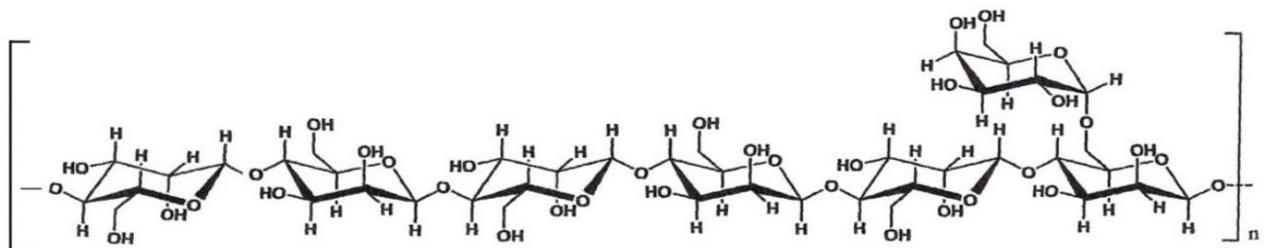
According to this new and widely accepted reclassification, we should better speak now of two different species *Senna tora* and *Senna obtusifolia* instead of *Cassia tora* and *Cassia obtusifolia*. Most of the botanists follow now this new classification.

Very likely *Senna tora* evolved within the plant evolution from *Senna obtusifolia*. *Senna obtusifolia* is in many respects highly variable, and *Senna tora* is highly invariable. As a result, *Senna obtusifolia* is widely distributed also in the New World. *Senna tora* shows a much narrower tolerance to seed storage temperatures.

As the seed germination is tolerant to a wide range of temperatures, *Senna obtusifolia* is a variable taxon, and it is not unlikely that it has given/will give rise to further new forms. Research on legumes goes on!

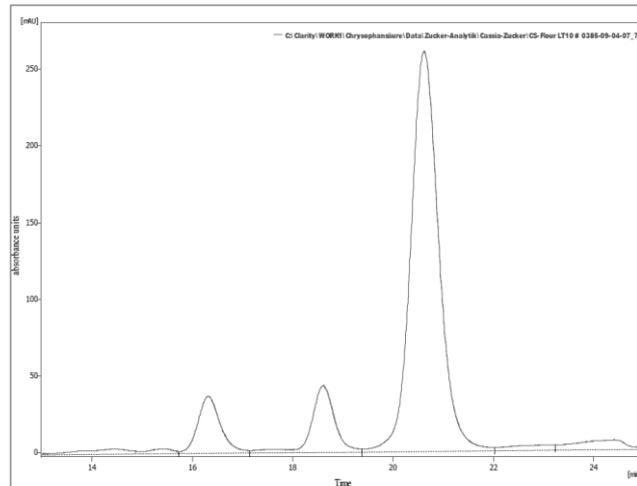
Nevertheless, the term *Cassia Gum*, referring to the polysaccharide isolated from the endosperm sections of the seeds of *Senna obtusifolia* and *Senna tora*, is widely accepted as a commercial item, well standardized within specified limits, and has found a common acceptance and a broad application in the relevant industries.

Over the years, we could never detect any differences between the galactomannan compositions of *Senna tora* and *Senna obtusifolia*. Accordingly, an idealised illustrative formula is suggested:



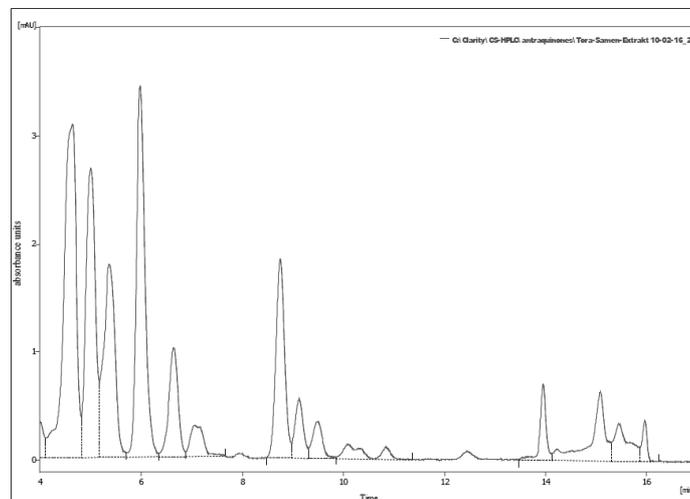
The statistic ratio of galactose to mannose is in average 1:5,5 to 1:6 within the standard deviation limits. Glucose is incorporated in the polysaccharide matrix of *Cassia gum* in nearly the same quantity as galactose, and is a fixed part of the specific *Cassia gum* polysaccharide matrix. The molecular weight cannot be differentiated between these two species (assessed at 200 -300 kDa).

A representative sugar chromatogram illustrating the sugar relations between mannose, galactose and glucose is shown hereunder.



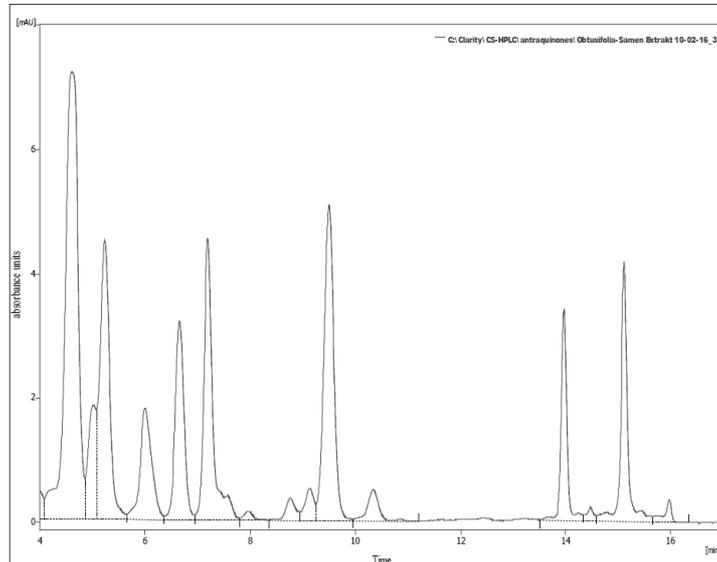
Research on fine structures of Cassia gum will go on.

Looking to the secondary plant metabolites as phytochemical tracer marks in *Cassia tora* and *Cassia obtusifolia* seeds, we find the most striking differences between these two species. Whereas *C. tora*, compared to *C. obtusifolia*, has a relatively high content of rubrofusarin and nor-rubrofusarin, the content of chryso-obtusin is nearly zero.



Also, the concentration of aurantio-obtusin and alaternin is much higher in *C. obtusifolia*. Worthwhile mentioning is also the lower ratio of chrysophanic acid to physcion in case of *C. tora*, compared to *C. obtusifolia*. This ratio reverses looking into the relevant glycosidic bound specimens. On the other hand, *C. obtusifolia* has a lower content of obtusin⁴ and a higher content of obtusifolin⁵ compared to *C. tora*.

Despite other findings published in the scientific literature, we never have found xanthorin in *Cassia tora* or *C. obtusifolia*. It seems, the examined samples of *Cassia tora* had been contaminated with *Cassia sophera* seeds, known to be rich in xanthorin.

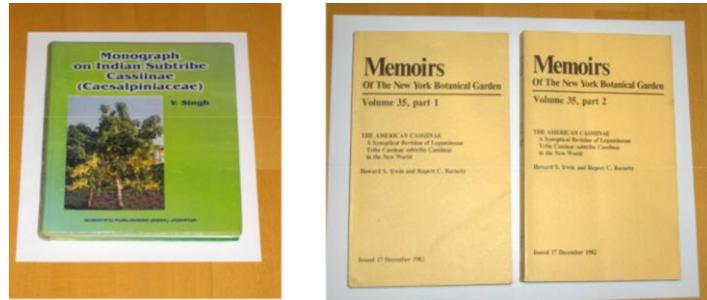


Accordingly, it is nowadays not difficult by means of relatively simple chromatographic equipment, even under isocratic conditions, to differentiate between these two species. What is valid for the aglycones is also true for the glycosidic bound polyketide derivatives. After enzymatic digestion or mild acid hydrolysis the aglycone pattern is a useful tool to identify *Cassia* seeds of various species.

Facing dwindling petroleum and natural gas based resources there is a must for the development of fast growing and yearly renewable plant materials with promising basic characteristics.

Encouraged by the economic progress of *C. obtusifolia* and *C. tora* plant material over the last 30 years, especially true for the endosperm, the polyketide metabolites or even the proteins, we strongly believe that the high variability of *C. obtusifolia* will generate future breeding and propagation experiments to increase the endosperm yield to a level of 45 to 50%, and also resulting in the isolation of industrially useful polyketide derivatives leading to anthraquinone and naphthopyrone specialties.

- 1) V. Singh, Monograph on Indian Subtribe Cassiinae (Caesalpinaceae) Journal of Economic and Taxonomic Botany, Additional Series No. 18



- 2) Howard S. Irwin and Rupert Barneby: Memoirs Of The New York Botanical Garden, Volume 35, part 1 and part 2
- 3) Dr. Barbara R. Randell, Taxonomy and evolution of *Senna obtusifolia* and *S. tora* J. Adelaide Bot. Gard. 16: 55 - 58 (1995)
- 4) Courtesy of Prof. Kim, Korean Institute of Oriental Medicine (KIOM), Deajeon, Korea
We are grateful to Professor Kim for a gift of 2.0 mg obtusin and 1.2 mg of rubrofusarin-6-O- β -D-gentiobioside
- 5) We wish to express our gratitude to Professor K. S. Song, Kyungpook National University, Daegu, Korea, for the generous gift of 1.4 mg obtusifolin.