Drug Development and Industrial Pharmacy, 2009; 35(6): 694–703

informa healthcare

ORIGINAL ARTICLE

Investigation of various shellac grades: additional analysis for identity

Karl Buch[1], Manfred Penning[2], Eva Wächtersbach[3], Michael Maskos[3] and Peter Langguth[1]

[1]*Department of Pharmaceutical Technology and Biopharmaceutics, Johannes Gutenberg-University, Mainz, Germany,* [2]*Pennconsult, Mainz, Germany and* [3]*Institute of Physical Chemistry, Johannes Gutenberg-University, Mainz, Germany*

Abstract

Background: A number of different grades of shellac are commercially available and most of them are known only as generic shellac and are not further differentiated. The investigated grades of shellac in this study are based on different insect strains, host trees, refining methods, and products from different suppliers. *Method*: The Gardner/Iodine color values of alcoholic and aqueous solutions of the various shellac grades were measured. Glass transition temperatures and pK_a-values were determined. To assess chemical differences in the tested shellac grades, MALDI-TOF analysis was performed. *Results*: Differences were found in color, T_G, and pK_a-values and in the mass spectra by MALDI-TOF analysis. *Conclusions*: The results indicate that these methods can facilitate the determination of identity and are quality control parameters for shellac.

Key words: *Coating; controlled release; identity; natural product; purity; shellac*

Introduction

The natural insect resin lac is known as shellac in the refined form. Under the general name shellac, many types or grades of shellac are commercially available. Their properties and color depend on the raw material (seedlac), the method for refining, and the processing parameters.

Because of its many technical applications, the color of the resin is often the main criterion for selecting a grade of shellac. Very often, raw materials are additionally mixed to achieve a certain color.

For controlled release applications, a light-colored resin is of interest; however, more important are the release characteristics and a constant quality of the selected grade.

While the various pharmacopoeias classify shellac according to the refining method, the only variable chemical property is the acid number. A narrow range of the acid number as well as a narrow specification of other physical properties like glass transition point and pK_a-value can be useful to achieve a constant quality.

The purpose of this article is to show that the properties of shellac depend on the raw material (seedlac), the refining process, and the processing parameters. Several shellac grades based on seedlac from various insect strains and refined by either the bleaching or solvent extraction process were investigated and characterized by several analytical methods including MALDI-TOF-MS. Orange shellac, refined by the melting process, was not included in the investigation because of the variations in raw materials, processing parameters, and batch to batch quality. Orange shellac is mainly used for technical applications.

In many, also recent, publications, only shellac or one specific grade of shellac was used for the investigation[1,2].

Cultivation and refining

Lac, a resinous secretion, is produced by the tiny insects *Kerria Lacca* (Kerr) Lindiger (Coccideae), which are parasitic on certain trees in India, Thailand, and southeast Asia[3]. Insects of the Kushmi strain are related to the Kusum tree (*Schleichera oleosa*), whereas insects of the

This article is dedicated to the late Dr. Walter Kalkhof-Rose, Honorary Senator of Johannes Gutenberg-University, Mainz, an outstanding chemist and industrialist in the field of shellac.

Address for correspondence: Professor Dr. Peter Langguth, Department of Pharmaceutical Technology and Biopharmaceutics, Johannes Gutenberg-University, Staudinger Weg 5, 55099 Mainz, Germany. E-mail: langguth@uni-mainz.de

(Received 2 Jun 2008; accepted 17 Oct 2008)

ISSN 0363-9045 print/ISSN 1520-5762 online © Informa UK, Ltd.
DOI: 10.1080/03639040802563253

Rangeeni strain (Bysakhi) habituate on the Palas (*Butea monosperma*) and Ber (*Zizyphus mauritiana*) trees. In Thailand, a slightly different species, *Laccifer chinensis* (Madihassan), habituates on the Raintree (*Samanea saman*). One insect strain is related to one type of tree only.

The insects pierce through the bark of the tree and transform the sap internally to a natural polyester resin, which is then secreted through the surface of the body. It is a by-product of the insects.

The resin forms thick encrustations on the twigs. The life cycle of the insects is approximately 6 months. After the swarming of the young insects, the resin is scraped off the twigs and further processed. Seedlac, as it is called at that stage, is then refined to become shellac.

The chemical composition, the properties, and the color of shellac depend on the insect strain or insect species and thus the host trees as well as the process used for refining (Table 1, Figure 1a–d).

Table 1. Insect strains in India and Thailand.

Crop	Insect strain	Host tree
Aghani, Jethwi	Kushmi	Kusum (*Schleichera oleosa*)
Bysakhi, Katki	Rangeeni	1. Palas (*Butea monosperma*)
		2. Ber (*Zizyphus mauritiana*)
Thai	Thai	Raintree (*Samanea saman*)

The life cycle of the insects is approximately 6 months. The Aghani and Bysakhi crops are the major crops in India.

Three very different processes (Figure 2) are used for refining seedlac to shellac[4], resulting in products with different chemical compositions, properties, and release characteristics[5].

Melting process

After melting the seedlac, the high viscous molten lac is pressed through a filter and drawn to a thin film on a

Figure 1. Trees: (a) Kusum tree, India (*Schleichera oleosa*); (b) Palas tree, India (*Butea monosperma*); (c) Ber tree, India (*Zizyphus mauritiana*); and (d) Raintree, Thailand (*Samanea saman*).

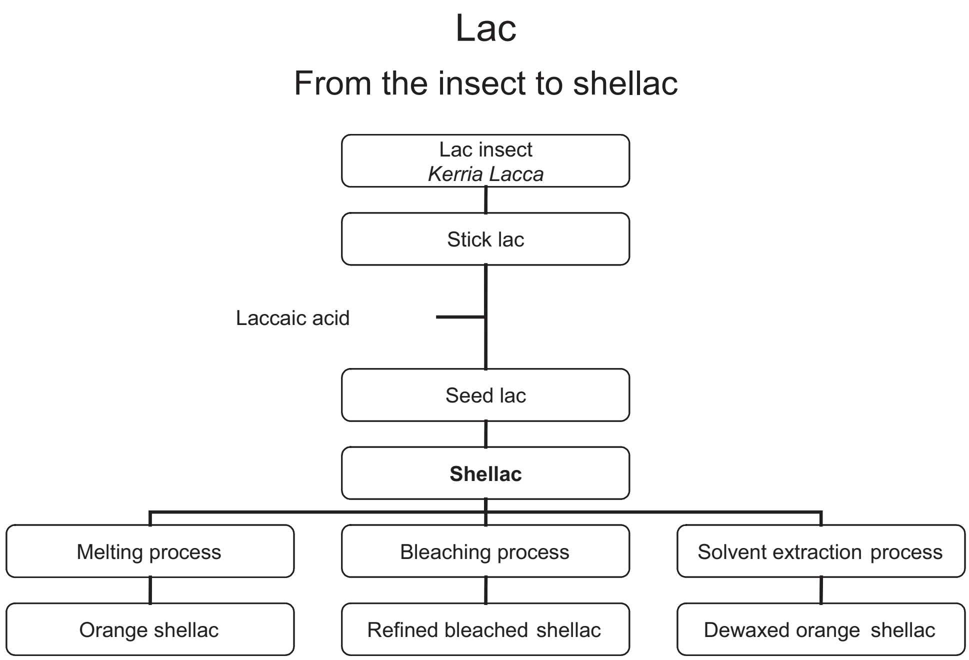

Figure 2. Flow chart demonstrating the refining process for shellac.

roller band. After cooling, the film breaks to small flakes. Shellac wax cannot be removed and the color depends on the seedlac used. This resin is mainly used for technical applications.

Bleaching process

For the purpose of bleaching, the seedlac is dissolved in an aqueous alkaline solution, filtered, dewaxed, and bleached with sodium hypochlorite to completely destroy the coloring matters of lac. Although this is an advantage for many technical applications, changes in the molecular structure and the addition of chlorine groups can lead to cross linking and polymerization. Batch to batch variations can be expected because of the variations in the raw materials used. Besides many technical and Do-it-yourself applications, bleached shellac is used for the coating of citrus fruits and apples as well as for confectionery and pharmaceutical glazes.

Solvent extraction process

Seedlac is dissolved in ethanol. Wax and impurities are removed by filtration. For light-colored grades, the color is reduced by treatment with activated carbon. Following a second filtration step and the stripping of the alcohol, the resin is drawn to a thin film which breaks into flakes upon cooling. The solvent extraction process is a very gentle process for refining shellac. However, the type of activated carbon and the processing parameters influence the properties of the final product.

Materials and methods

Materials

The various grades of shellac were samples received from the respective manufacturers or distributors. SSB 55, SSB 57—Ber, SSB 57—Palas, SSB 61, and Dreiring Pharma were supplied from Stroever GmbH & Co. KG (Bremen, Germany). Pearl-N811F and Pearl-N811Ph were obtained from Gifu Shellac Co. Ltd. (Gifu, Japan). Shellac DBL and AT 10–1010 were obtained from Alltec Intertrade (Ganderkesee, Germany). These data are summarized in Table 2.

All other reagents used were of analytical grade and used as received.

Methods

Gardner color/Iodine color

All measurements were done using the color tester Lico 50 (Dr. Lange GmbH, Düsseldorf, Germany) in 11-mm cylindrical glass cuvettes. The measuring principle is a photometric method. Light transmitted through the sample is fractionized by filters and the intensity measured by photosensors in comparison to a reference beam. The different shellac grades were dissolved in ethanol 96% at a concentration of 20% (m/V)[6]. Aqueous shellac solutions (20%, m/V) were prepared as follows: An amount of ammonium hydrogen carbonate, which is needed to neutralize the acid groups of shellac, was dissolved in deionized water, shellac was added, and the

Table 2. Overview of investigated shellac grades.

Trade name	Manufacturer	Supplier	Seedlac type	Refining method
SSB 55	Stroever GmbH & Co. KG, Bremen, Germany	Stroever GmbH & Co. KG, Bremen, Germany	Kushmi	Solvent extraction
SSB 57—Ber	Stroever GmbH & Co. KG, Bremen, Germany	Stroever GmbH & Co. KG, Bremen, Germany	Bysakhi—Ber	Solvent extraction
SSB 57—Palas	Stroever GmbH & Co. KG, Bremen, Germany	Stroever GmbH & Co. KG, Bremen, Germany	Bysakhi—Palas	Solvent extraction
SSB 61	Stroever GmbH & Co. KG, Bremen, Germany	Stroever GmbH & Co. KG, Bremen, Germany	Thai seedlac	Solvent extraction
Pearl-N811F	Gifu Shellac Mfg. Co., Ltd., Gifu, Japan	Gifu Shellac Mfg. Co., Ltd., Gifu, Japan	Thai seedlac	Solvent extraction
Pearl-N811Ph	Gifu Shellac Mfg. Co., Ltd., Gifu, Japan	Gifu Shellac Mfg. Co., Ltd., Gifu, Japan	Thai seedlac	Solvent extraction
Dreiring Pharma	Stroever GmbH & Co. KG, Bremen, Germany	Stroever GmbH & Co. KG, Bremen, Germany	Thai seedlac	Bleaching process
Shellac DBL	Tajna River Ind. Pvt. Ltd., Ranchi, India	Alltec Intertrade, Ganderkesee, Germany	Indian seedlac	Bleaching process
AT 10–1010	Hindustan Shellac Pvt. Ltd., Howrah, India	Alltec Intertrade, Ganderkesee, Germany	Kushmi	Solvent extraction

dispersion heated to 70°C and stirred for half an hour until a clear solution was formed. The pH of all aqueous solutions was between 7.0 and 7.3.

Glass transition temperatures

All samples were analyzed using a Mettler Toledo DSC 30. The data were analyzed using Mettler Graphware software. The DSC was calibrated against indium as temperature and enthalpy standard. Each sample (9–10 mg) was accurately weighed into a 30-µL aluminium pan, the caps were perforated once, and the samples directly measured. The samples were heated at 10°C/min from –30°C up to 200°C with 80 mL/min of nitrogen purge. Glass transition temperatures (T_G) are reported as the turning point of the curve progression.

Determination of pK_a-values

pK_a-values were determined using the Parke-Davis-method[7] with slight modification[8].

Shellac (0.5 g) was dissolved in 25.0 mL of a 0.1 N solution of sodium hydroxide in water and heated gently until shellac was totally dissolved. Shellac solution was then cooled to room temperature and titrated with a solution of 0.1 N hydrochloric acid. A Qph 70 ph-meter (VWR International, Darmstadt, Germany) was used to measure pH-values. A reference without shellac was titrated, and the data were plotted as pH versus volume of titrant solution. The difference curve is obtained by subtraction of the shellac curve from the reference curve, that is, by the differential formed by subtraction of the volume of 0.1 N hydrochloric acid needed to reach a specific pH-value between the shellac and the blind curve. The subtraction is done with QUIDAS software after interpolation via B-splines. The difference curve obtained is subsequently normalized to titration grades from $\tau = 0$ to $\tau = 1$. pK_a-values are the intersections of a curve with the x-axis at $y = 0$ after a plot of log $[(1 - \tau)/\tau]$ against pH; in this point of the curve pH equals the pK_a-value.

MALDI-TOF-MS

The MALDI-TOF-MS analysis was performed using a TofSpecE Analyzer (Micromass, Manchester, UK). Samples were prepared as follows[9]. Shellac was dissolved in 100% ethanol at a final concentration of 1% (m/v). This fresh ethanolic solution (20 µL) was mixed with 20 µL DHB-matrix solution, consisting of 2.5-dihydroxybenzoic acid in ethanol and 0.1% trifluoroacetic acid. About 2 µL of this shellac-matrix solution was deposited on the target plate and dried at room temperature. Screening of the shellac samples was performed in reflector mode.

Results and discussion

Color

In the current European Pharmacopoeia 6.2, shellac appearance is described as brownish-orange or yellow, shining, translucent, hard or brittle, more or less thin flakes. Bleached grades of shellac in contrast are much lighter and are available as creamy white or brownish-yellow powder. Shellac, in general, is mostly used as coating material—therefore the color plays an important role. In the past, the color was often the main factor for choosing a specific grade of shellac.

The variability in the appearance of the tested ammoniated aqueous shellac solutions is shown in

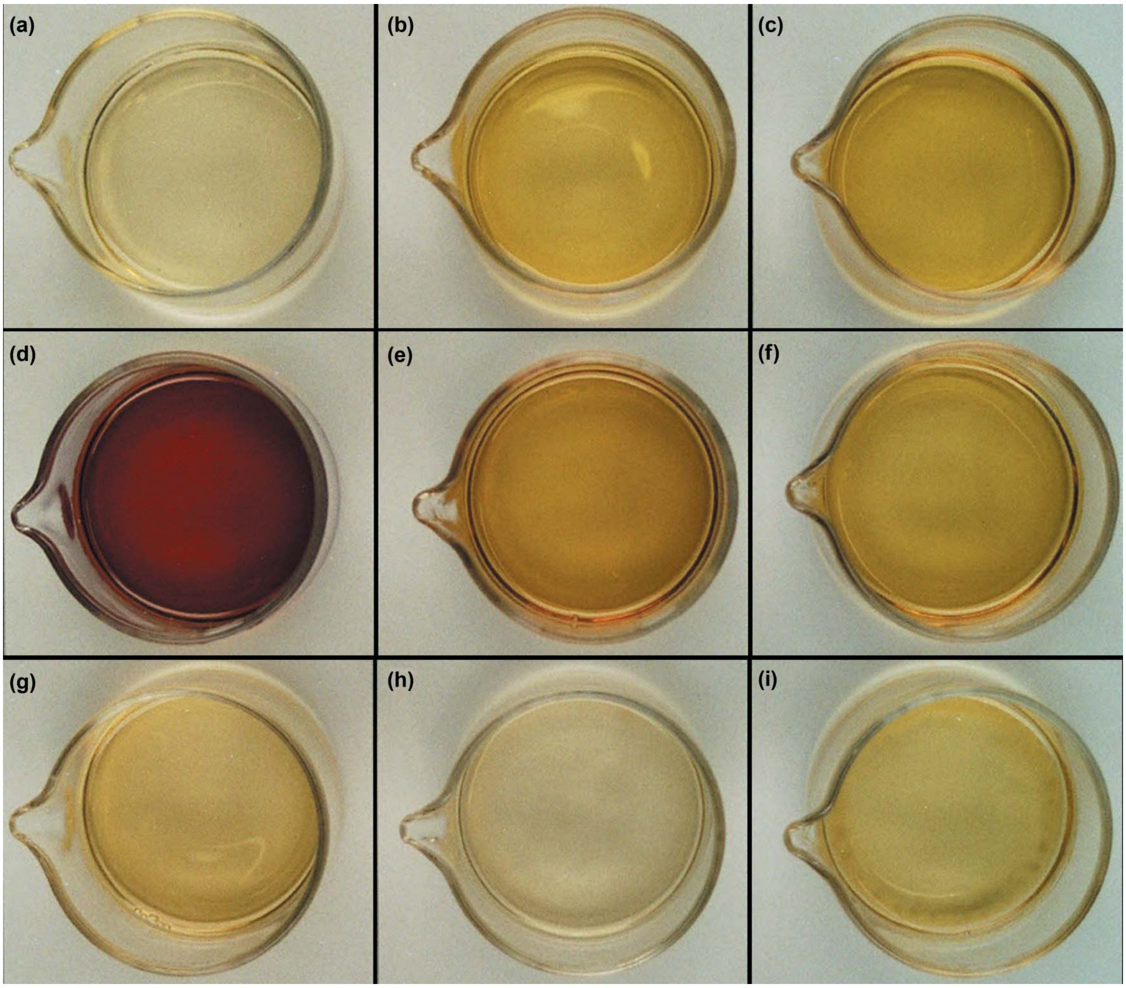

Figure 3. Ethanolic solutions of tested Shellac grades (20%, m/V). (a) SSB 55, (b) SSB 57—Ber, (c) SSB 57—Palas, (d) SSB 61, (e) Pearl-N811F, (f) Pearl-N811Ph, (g) Dreiring Pharma, (h) Shellac DBL, and (i) AT 10-1010.

Figure 3. Bleached shellac samples are Dreiring Pharma and Shellac DBL, all other grades were refined by solvent extraction.

In addition to the visual appearance, aqueous and ethanolic solutions of shellac were evaluated by the color numbers according to Gardner and Iodine. The results are listed in Table 3.

SSB 61 is the darkest shellac in this investigation; its color number is too high to be measured by our equipment. Gardner color numbers from all other shellac grades were in a range from 5.8 to 10.3 for ethanolic solutions, whereas fresh aqueous shellac solutions were in a range from 8.3 to 11.9. Iodine color numbers were in a range from 7.5 to 97.9.

Shellac grades based on Kushmi or Bysakhi seedlac have lower color numbers in comparison to shellac grades based on Thai seedlac. Possible reasons are process parameters of the refining process commonly made with activated carbon, where the color can be adjusted to the desired values. Bleached grades such as Dreiring Pharma and Shellac DBL show lower color numbers because of the destruction of the color system by bleaching.

Table 3. Color numbers of different shellac grades (solutions measured immediately after preparation).

	Ethanolic solution 20%		Aqueous solution 20%	
Shellac grade	Gardner	Iodine	Gardner	Iodine
SSB 55	5.8	7.5	8.3	23.3
SSB 57—Ber	8.6	28.9	10.3	58.6
SSB 57—Palas	9.2	39.5	10.8	71.7
SSB 61	—	—	—	—
Pearl-N811F	10.3	58.6	11.9	97.9
Pearl-N811Ph	9.0	35.8	10.5	64.4
Dreiring Pharma	7.3	14.3	9.1	38.3
Shellac DBL	6.5	10.8	8.8	30.7
AT 10–1010	8.0	18.3	8.5	26.8

Because of range of the color tester, the color number of SSB 61 could not be measured.

Pearl-N811Ph is also slightly lighter than Pearl-N811F, corresponding to more specific requirements for shellac of pharma quality, because dark coatings are less accepted for pharmaceutical applications.

Darkening of some of the ammoniated aqueous shellac solutions after storage was observed as can be seen in Table 4, where color numbers are shown after storage at room temperature for 29 days. Visual darkening of ethanolic solutions was not observed in this study and is normally not noticeable[10].

Bleached grades of shellac show a higher degree of darkening. In particular, Dreiring Pharma shows a much higher darkening than all unbleached grades. Only Shellac DBL shows no significant increase in its color number. Darkening of ammoniated aqueous solutions is caused by the content of chlorine groups in shellac[9] and the parameters of the bleaching process. It should be mentioned that bleached shellac, because of variations in raw materials and processing parameters, can have batch to batch variations in release characteristics.

Physicochemical properties

Thermal behavior of shellac was investigated by the determination of glass transition temperature (T_G) via differential scanning calorimetry. Determination of glass transition temperature is mostly related to glasses or polymeric substances. Despite the fact that shellac consists mostly of monomeric and oligomeric compounds as the MALDI measurements showed, glass transition can be observed. Shellac below its T_G-value is a hard amorphous substance and above its T_G-value shellac becomes soft and capable of plastic deformation without fracture. As it can be seen in Table 5, all T_G-values are in a range between 35°C and 52°C.

All shellac grades showed relatively similar thermal behavior. The onset in the step of glass transition is clearly noticeable. SSB 55, based on Kushmi seedlac, has the lowest T_G (35°C). Both shellac grades based on Bysakhi seedlac, SSB 57—Ber and SSB 57—Palas, show a T_G of 39°C and 40°C. Shellac grades, based on Thai seedlac, show T_G-values in a range of 39.5°C for SSB 61, 41°C for Pearl-N811F, and 52°C for Pearl-N811Ph. As already seen in the optical properties, there is again a difference between Gifu Shellac in food and pharma grades. The T_G of AT 10–1010, refined by solvent extraction and based on Kushmi, is with 52°C considerably higher than SSB 55.

Table 4. Color numbers of different shellac grades (29 days old solution).

	Aqueous solution 20%	
Shellac grade	Gardner	Iodine
SSB 55	8.8	31.8
SSB 57—Ber	10.6	64.8
SSB 57—Palas	11.3	85.0
SSB 61	—	—
Pearl-N811F	—	—
Pearl-N811Ph	11.0	76.7
Dreiring Pharma	10.5	62.6
Shellac DBL	8.8	32.5
AT 10–1010	8.6	29.3

Because of the range of the color tester, SSB 61 and Pearl-N811F could not be measured.

Table 5. Glass-transition temperatures of different shellac grades.

Shellac grade	T (°C)
SSB 55	35
SSB 57—Ber	39
SSB 57—Palas	40
SSB 61	39.5
Pearl-N811F	41
Pearl-N811Ph	52
Dreiring Pharma	48
Shellac DBL	49
AT 10–1010	52

Bleached shellac grades, such as Dreiring Pharma and Shellac DBL, also show relatively high T_G-values of 48°C and 49°C, their T_G-values are in general higher than those of unbleached shellac grades. Pearl-N811Ph and AT 10–1010 also show higher T_G-values, which is probably due to differences in activated carbon and different processing parameters during refining.

Chemical properties

Shellac in pharmaceutical applications is used as coating material for controlled release of enteric-coated dosage forms such as soft-gelatine capsules, hard-gelatine capsules, tablets, or pellets[11,12]. It is known[13] that pK_a-values are important for the characteristics of dissolution behavior of shellac-coated products[14]. Therefore, its chemical properties such as acid number and pK_a-values that relate to its functions have been characterized in this work.

The pK_a-values of the different shellac types investigated varied in a range between 5.60 and 6.59 (Table 6). The shellac grades from Stroever (SSB 55, SSB 57—Ber, SSB 57—Palas, and SSB 61) are relatively similar, only SSB 57—Palas shows a higher pK_a compared with 6.11 for SSB 55, 6.24 for SSB 57—Ber, and 6.20 for SSB 61. Differences between Stroever grades are because of different raw materials such as Kushmi seedlac, Bysakhi seedlac, and Thai seedlac, but the refining process parameters, different types of activated carbon, and differences in the duration of the treatment with activated carbon during refining by solvent extraction play an important role as well.

Table 6. pK_a-values of different shellac grades and their acid number (according to certificate of analysis).

Shellac grade	pK_a	Acid number
SSB 55	6.11	73
SSB 57—Ber	6.24	74
SSB 57—Palas	6.59	74
SSB 61	6.20	67
Pearl-N811F	6.13	70.9
Pearl-N811Ph	5.96	71.1
Dreiring Pharma	5.60	79
Shellac DBL	5.64	93
AT 10–1010	6.15	74

Particularly, the difference in pK_a between SSB 57—Ber and SSB 57—Palas is remarkable, because this shellac is based on the same insect strain (Bysakhi), probably refined with similar process parameters, with very similar glass transition temperature (39°C and 40°C), nearly with the same color properties and even with identical acid numbers (74).

The pK_a-values from Gifu Shellac grades varies from 6.13 (food grade) to 5.96 (pharma grade). The latter because of its application purposes is somewhat less colored but shows an equal acid number compared to the food quality (70.9 versus 71.1). Remarkable is the gap in the glass transition temperature of 11°C between Pearl-N811F and Pearl-N811Ph, which may be caused by changes in the refining process parameters. In addition, there are differences found by MALDI-TOF in these shellac grades.

Both bleached shellac grades (Dreiring Pharma and Shellac DBL) show, with 5.60 and 5.64, respectively, even the lowest pK_a-values. The pK_a-values of bleached shellac, in general, are lower than those of shellac refined by solvent extraction.

In order to determine varieties in the chemical structure of shellac and differences between different shellac grades, MALDI-TOF-MS analysis was performed with the various shellac samples. Figure 4 shows a mass spectrum of sample SSB 57—Ber. MALDI-TOF spectra of the other samples appear very similar, only small differences are identified.

As expected, the mass spectrum is of very complex structure. In the mass range of m/z 500–2000, five major groups of ions are found, which represent the extent of polymerization. Minor ion groups above m/z 1800 are also detected. Thus, MALDI-TOF mass spectra are able to provide information about the chain length distribution as well as structured heterogeneity of the natural polymer. MALDI-TOF generates good mass spectra in the middle mass range of the shellac of about m/z 500–1200. The five major ion groups represent polymerized constituents of shellac in the range from monomers to tetramers along with hydroxyl fatty acids. MALDI-TOF produces mostly $[M+Na]^+$ ions from shellac samples. Peaks that belong to the DHB matrix have to be subtracted. Therefore, a blank sample run was done, only with matrix, but without shellac.

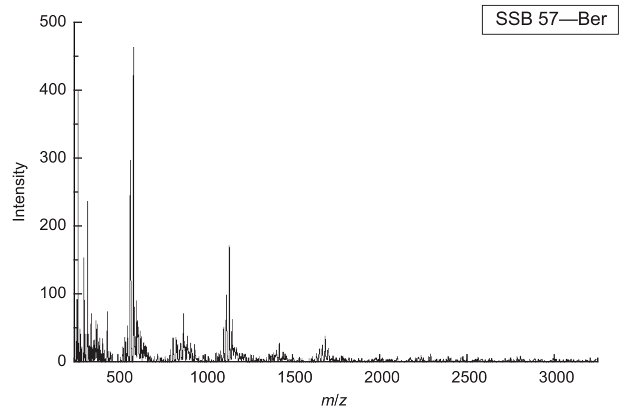

Figure 4. MALDI-TOF mass spectrum of SSB 57—Ber.

Structures of shellac components reported in the literature[15] that were used as starting point for identifying peaks in mass spectra are listed in Table 7; their chemical structure can be seen in Figure 5.

In all mass spectra, peaks in the range of aleuritic acid (m/z 304) were recognizable but very weak, which indicates low content of free aleuritic acid. The same holds true for free shellolic acid and free jalaric acid. Mass ions of hydroxyl fatty acids below m/z 280 are observed but not further identified; for that purpose other analytical techniques have to be employed.

Figure 6 shows sections of the MALDI-TOF mass spectra. At the low end of the spectrum at m/z 589 and m/z 605, respectively, the fragmentation pattern indicates the presence of monomeric or single-ester components of the shellac resin with the m/z 589 consisting of an aleuritic acid (A) and a jalaric acid (J), or its possible isomers,

Table 7. Masses of assumed constituents in shellac.

Name	Mass (g/mol)
Monomeric constituents	
Aleuritic acid (A)	304
Shellolic acid (S)	296
Jalaric acid (J)	280
Chemical compounds (esters)	
AJ	566
AS	582
AJA	852
ASA	868
AJAJ	1114
AJAS	1130
ASAS	1146
AJAJA	1400
AJASA	1416
ASASA	1432

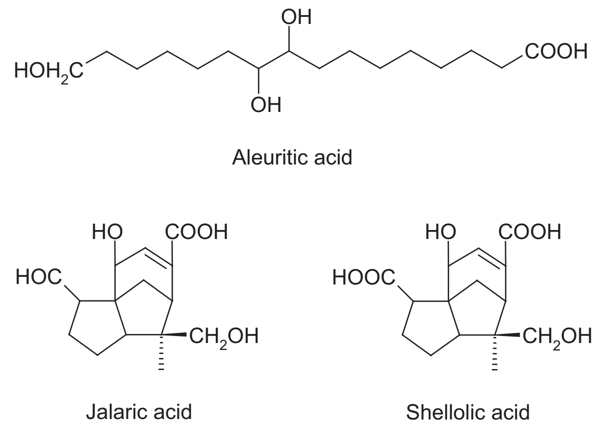

Figure 5. Chemical structures of main shellac components.

and m/z 605 consisting of an aleuritic acid (A) and a shellolic acid (S), or its isomers. Peaks in shellac samples at m/z 875 are caused by structures of AJA or AAJ species; peaks at m/z 891 may be derived from structures like ASA or AAS (see Table 7 for the abbreviation). Species of AJAJ nature are proposed to result in peaks of m/z 1137, species of AJAS in m/z 1153, and species of ASAS in m/z 1169. As can be seen in Figure 6, all of these peaks can be identified in the mass spectra of the shellac samples, but the height of the peaks that relates to the different quantities is not distributed equally.

It can also be seen from Figures 4 and 6 that additional peaks exist, which could not be identified at present. Noticeable is a peak of m/z 623 in the Dreiring Pharma and Shellac DBL samples, which is only explainable by the assumption of a structure such as AJ with a chlorine atom within the molecule. This is because of the fact that these shellac grades are bleached with sodium hypochlorite. Further peaks at m/z 909, m/z 1171, and m/z 1187 are based on molecules with chlorine atoms, that is, AJA-Cl, AJAJ-Cl, and AJAS-Cl, respectively. These peaks are very useful to differentiate between bleached and unbleached grades or to detect mixtures of bleached and unbleached shellac grades.

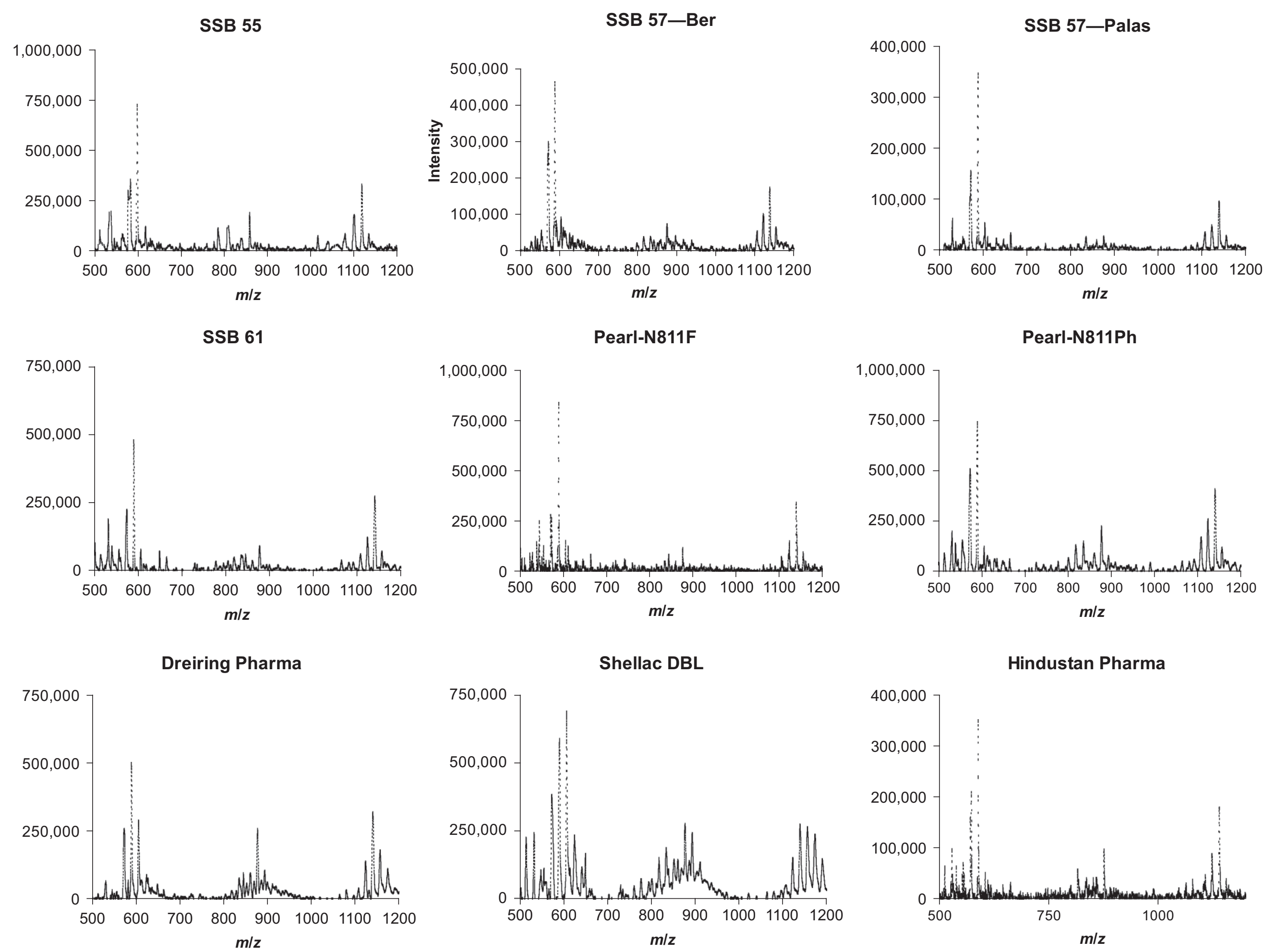

Figure 6. Mass spectra of shellac grades (section of m/z 500–1200).

Another difference is based on different ratios of AJ to AS. In shellac grades except for SSB 57—Palas, Dreiring Pharma, and Shellac DBL, the amount of AJ is about six times higher than the amount of AS. In SSB 57—Palas, the amount of AJ is seven times higher than AS. In Dreiring Pharma, bleached shellac, the amount of AJ is only 1.7 times higher than the amount of AS; in Shellac DBL, slightly higher amounts of AS than AJ were found.

The ratio of m/z 1137 (AJAJ) to m/z 1153 (AJAS) is about 3–4:1 in all shellac samples, except for the bleached grades. In Dreiring Pharma only 50% more AJAS than AJAJ was found, and in Shellac DBL the amount of these components is nearly equal.

A difference was also found between bleached shellac grades in terms of the height of the signal at m/z 1187 (AJAS-Cl), which in Shellac DBL is much higher than in Dreiring Pharma. This is because of the fact that the content of unchlorined AJAS in this sample is also higher, indicating that these peaks are helpful to differentiate between bleached and unbleached shellac grades.

The mass spectrum of Pearl-N811F in comparison to the spectrum of Pearl-N811Ph shows more compounds that are of monomeric or dimeric origin. No mass peaks above m/z 2300 could be detected in Pearl-N811F, but there are a few peaks in the spectrum of Pearl-N811Ph, which indicate the presence of higher molecular weight compounds of shellac. This fact could be an explanation for the differences in thermal behavior, specified in glass transition temperature.

These phenomena could also be a possible explanation for differences in T_G-values of other tested shellac grades. Pearl-N811Ph as well as AT 10–1010 and also both bleached grades Dreiring Pharma and Shellac DBL have T_G-values in a range of 48–52°C. In all these grades, MALDI-TOF spectra show much more peaks of higher masses compared to SSB 55. SSB 55 also shows peaks at m/z 1973 or 2236, but these peaks are fewer and their signal is lower.

In order to distinguish between several shellac grades in detail, small differences in mass spectra have to be analyzed. Some of the numerous mass peaks are able to distinguish between several shellac grades. A peak at m/z 1973 (AJAJAJA) is only recognizable in SSB 55, SSB 61, Pearl-N811F, Pearl-N811Ph, Dreiring Pharma, Shellac DBL, and AT 10–1010 but neither in SSB 57—Ber nor in SSB 57—Palas.

A pair of two peaks at m/z 2236 and 2293 gives further help for identifying. Peak m/z 2236 is detectable in all grades, whereas the peak at about m/z 2293 is only in spectra of SSB 57—Ber and both bleached grades detectable. In Shellac DBL, the peak at m/z 2293 is in almost the same height apparent in comparison to the peak at m/z 2236.

Shellac DBL shows a special peak characteristic; there are three peaks at m/z 572, 590, and 606 in ascending signal height. This composition is unique in tested shellac grades, hence clearly an identifier.

Conclusions

Shellac is a very complex mixture of mainly aliphatic and alicyclic acid components. Because of insect strain and refining method, variations in composition and appearance are noticeable. Some differences are obvious, such as color numbers of the different grades. The values given in this article present objective values and allow a first identification of an unknown shellac grade. Results of measured glass transition temperatures provide further opportunity to differentiate between bleached and unbleached shellac grades, between food and pharma grades (Pearl-N811), or between SSB 55 and AT 10–1010.

Bleached shellac grades show the lowest pK_a-values, but there are also differences between shellac grades based on Thai seedlac, Kushmi seedlac, and Bysakhi seedlac, which may be of interest for the dissolution behavior of coated products. This will be reported in a future communication.

Beside the various seedlac types, the influence of different activated carbons and processing parameters during solvent extraction of the shellac refiner is important. It is suggested to define the various shellac grades by acid number, T_G- and pK_a-values.

MALDI-TOF-MS has proven to be a powerful technique to provide detailed information about the molecular structure of shellac components. Our results show the presence of a wide range of shellac components with groups of single acids at the lower mass scale and polyesters up to tetramers at higher masses. The use of MALDI-TOF-MS further allows to distinguish unbleached from bleached shellac grades and also between the various grades of shellac refined by solvent extraction.

Declaration of interest: The authors report no conflicts of interest.

References

1. Pearnchob N, Dashevsky A, Siepmann J, Bodmeier R. (2003). Shellac used as coating material for solid pharmaceutical dosage forms: Understanding the effects of formulation and processing variables. STP Pharm Sci, 13(6):387–96.
2. Pearnchob N, Siepmann J, Bodmeier R. (2003). Pharmaceutical applications of shellac: Moisture-protective and taste-masking coatings and extended-release matrix tablets. Drug Dev Ind Pharm, 29(8):925–38.
3. Mukhopadhyay B, Muthana MS. (1962). A Monograph on lac. Howrah: Glasgow Printing Company Private. Ltd.

4. Penning M. (1990). Schellack – ein nachwachsender Rohstoff mit interessanten Eigenschaften und Anwendungen. Seifen – Öle – Fette – Wachse, 1990(6):221–4.
5. Penning M. (1996). Aqueous shellac solutions for controlled release coatings. In: Karsa DR, Stephenson RA, eds. Chemical aspects of drug delivery systems. Royal Society of Chemistry, 178:146–54.
6. Angelo Brothers Limited. (1965). Shellac. Calcutta, India: Cossipore.
7. Parke TV, Davis WW. (1954). Use of apparent dissociation constants in qualitative organic analysis. Anal Chem, 26(4):642–5.
8. Riedel A. (2005). Interaktionen zwischen Kernbestandteilen und Filmüberzügen und ihre Auswirkung auf die Wirkstofffreisetzung aus magensaftresistent überzogenen Arzneiformen. Berlin: Logos-Verlag.
9. Tang, J. (2003). Characterization of Shellac by MALDI-TOF-MS, ESI-TOF-MS and MS-MS. Poster MPP 301, 51st ASMS Meeting, Montreal.
10. Marx EL. (1964). Die wichtigsten Kennzahlen von Schellack und deren Bestimmung. Deutsche Farben-Zeitschrift, 18(8):347–51.
11. Specht F. (1998). The Application of shellac as an acidic polymer for enteric coating. Pharm Technol Eur, 10:20–8.
12. Luce GT. (1978). Disintegration of tablets enteric coated with CAP (cellulose acetate phthalate). Manuf Chem Aerosol News, 49(50):50.
13. Signorino C. (2003). United States Patent No. 6620431.
14. Chambliss WG. (1983). The forgotten dosage form: Enteric coated tablets. Pharm Technol, 7(9):124–40.
15. Wang L, Ishida Y, Ohtani H, Tsuge S, Nakayama T. (1999). Characterization of natural resin shellac by reactive pyrolysis-gas chromatography in the presence of organic alkali. Anal Chem, 71(7):1316–22.