

Tracing colophonium in consumer products

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Abstract

Background

Colophonium (rosin) can cause allergic contact dermatitis, mainly due to autoxidation of abietic acid (AbA). Products containing $\geq 0.1\%$ colophonium should be labelled with EUH208 — 'Contains rosin; colophony. May produce an allergic reaction'. How should this be measured?

Objective

To compare the results from different strategies for estimating colophonium levels in consumer products: 1) from AbA, and 2) the sum of all major resin acids. To investigate the ratio 7-oxodehydroabietic acid (7-O-DeA)/AbA as indication of autoxidation.

Methods

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Resin acids were extracted from consumer products, derivatized and then separated by gas chromatography/mass spectrometry (GC/MS).

Results

Resin acids were detected in 9/15 products. No product contained colophonium ≥ 0.1 %. Estimation based on AbA resulted in underestimation of the colophonium levels in 4/9 products. For three products the obtained levels from this strategy were only 1/2 compared to when estimating from the sum of all resin acids. The ratio 7-O-DeA/AbA varied from 74 % - 1.4 %.

Conclusions

We propose to measure colophonium based on the sum of all detectable major resin acids, including 7-O-DeA. The ratio 7-O-DeA/AbA should be used as a marker of autoxidation, indicating an increased risk of sensitization. The presented analytical method is simple to use and suitable for further screening studies.

1. Introduction

Colophonium (rosin, CAS 8050-09-7) is still a common cause of contact allergy in the general population as well as of occupational contact dermatitis. A prevalence of 0.9 % of contact allergy in the general population was assumed based on patch testing 3119 individuals in five European countries with colophonium from the True test panel during the years 2008-2011.¹ Between 1.4 and 4.2 % has been reported for consecutively patch tested dermatitis patients in Europe.²⁻⁴

Colophonium/rosin has a harmonised classification (included in CLP Annex VI, legally binding) as a *skin sensitizer in category 1*. Products containing at least 1% rosin must be classified and labelled as 'H317: May cause an allergic skin reaction'. Mixtures containing rosin at a concentration of at least 0.1% should be labelled with the statement EUH208 — 'Contains rosin; colophony. May produce an allergic reaction' and a safety data sheet is required. (REGULATION (EC) No 1272/2008 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006). To the best of our knowledge no standardized analytical method for colophonium *per se* is so far present

for consumer or technical products. The published analyses identify and often quantify various prominent resin acids present in unmodified colophonium, but do not quantify colophonium *per se*. To the best of our knowledge, estimations have been made in only two publications, connecting the detected concentration of the major resin acid, abietic acid (AbA), with a total concentration of colophonium in various technical products.^{5,6}

Colophonium is a highly complex natural product and the chemical composition varies depending on the origin and production. Three major types exist: gum rosin, tall oil rosin and wood rosin of which the first two are commercially most important. Colophonium is used in its entirety without further fractionation, but depending on production, handling and storage, the relative content of resin acids varies. About 90 % of the natural product consists of resin acids of abietane- or pimarane-type structures (Fig 1), while approx. 10 % consists of a neutral fraction. The major abietic-type acid for gum rosin is AbA and for tall oil the main component is dehydroabietic acid (DeA).

Colophonium is widely used as an adhesive and water-resistant material in industrial processes as well as in numerous consumer products. A thorough review of colophonium in terms of usage, exposure, prevalence of contact allergy and cases of allergic contact dermatitis is given in Karlberg and Hagvall from 2018.⁷ It has been shown that the major skin-sensitizing compounds are the oxidized abietic-type acids.⁸⁻¹² In contact with air, AbA readily forms skin-sensitizing oxidation products, such as 15-hydroperoxyabietic acid (15-HPA)⁸, the major allergen, and related secondary oxidation products, such as 7-oxo-dehydroabietic acid (7-O-DeA).⁹ The minor neutral fraction of gum rosin can form allergens after autoxidation.^{13,14} Colophonium is modified to a large extent to obtain suitable technical qualities. Modifications and derivatizations, mainly of the abietic-type acids, change the composition and can create new skin sensitizers such as maleopimaric acid.¹⁵ However, there is always a small amount of unmodified resin acids left.⁷

A literature review of analytical methods for identification and quantification of specific resin acids in colophonium/rosin in technical products is included in a report from the Danish Ministry of the Environment in 2009.¹⁶ To our knowledge, very few studies have been published since then on the identification of resin acids in consumer products. In an article from 2016, the content of resin acids was quantified in sized paper products

using high-performance liquid chromatography/ultraviolet detection (HPLC/UV) after alkali treatment.¹⁷ The resin acids were quantified together in one HPLC fraction using a wavelength where the extinction coefficients are the same. The most common published analytical methods have so far been HPLC/UV or gas chromatography/flame ionization detection (GC/FID). HPLC is more straightforward since the extracts can be analyzed directly without derivatization. Free resin acids can also be separated and detected by HPLC/atmospheric pressure chemical ionization (APCI)-mass spectrometry (MS)¹⁸ or HPLC/electrospray ionization-mass spectrometry (ESI-MS).¹⁹ GC yields more efficient chromatographic separation of the complex composition, but requires derivatization such as alkylation or silylation. GC/FID and GC/MS have been used since long in the papermaking industry for monitoring resin acids in process waters. A thorough review of analytical methods for resin acids in these matrices was published in 2012.²⁰

Apart from chromatography and detection, an important part of the analytical method for consumer products is the cleanup method to enable analysis of the components in a suitable matrix. Most methods have so far been liquid-liquid extraction, but with solid-phase extraction (SPE) the selectivity can be more fine-tuned for resin acids. We have previously developed a highly selective mixed-mode anion-exchange SPE method for quantification of AbA, DeA and 7-O-DeA in consumer products.²¹ In the present paper, we have combined this SPE method for enrichment of resin acids followed by derivatization and GC/MS^{22,23} for a comprehensive quantification of all major resin acids of both abietic-type and pimaric-type from unmodified colophonium in some representative consumer products. The quantification also included 7-O-DeA. As AbA oxidizes at air exposure it is important to include detection and quantification of stable oxidation products, such as 7-O-DeA. Otherwise, the concentration of AbA will be underestimated. The ratio between 7-O-DeA and AbA can also indicate the status of oxidation of colophonium. We have in previous work quantified AbA, DeA and 7-O-DeA as markers of colophonium in cosmetics, diapers and footwear.^{21,24,25}

In the present study, the choice of products was based on our earlier analyses and results. The aim was to investigate the difference in colophonium content dependent on which colophonium components the estimation is based on (either the sum of all

detected resin acids or only AbA). Another objective was to point at the need for a validated standardized analytical method for colophonium measurements, including cleanup, separation and detection of specific colophonium components in consumer and technical products. A suggestion is to define the colophonium level in the product as the sum of all major resin acids from unmodified rosin, plus an estimated neutral fraction (10%). The stable oxidation product from AbA, 7-O-DeA should be included in the quantification to add to the concentration of AbA, but also as a marker of oxidation.

2. Materials and Methods

2.1 Chemicals and materials

Acetonitrile, methanol, acetone, and toluene were all of HPLC grade and were purchased from Rathburn Chemicals Ltd (Walkerburn, Scotland). Derivatization reagent, 2,3,4,5,6-pentafluorobenzyl bromide (PFBBBr, 99%) was obtained from Sigma-Aldrich (Schnelldorf, Germany), sodium acetate (99.9%) from VWR Chemicals (Darmstadt, Germany), triethylamine ($\geq 99\%$) from Sigma-Aldrich (Overijse, Belgium), and formic acid ($\geq 98\%$) from Sigma-Aldrich (Munich, Germany). Ultrapure water with a resistivity of 18.2 M Ω cm was produced in-house by using a Milli-Q[®] equipment from Merck (Darmstadt, Germany).

Abietic acid (AbA, 95%, CAS 514-10-3), palustric acid (PaA, 90%, CAS 1945-53-5), neoabietic acid (NeoA, 99%, CAS 471-77-2), dehydroabietic acid (DeA, 99%, CAS 1740-19-8), pimaric acid (PimA, 95%, CAS 127-27-5), isopimaric acid (IsoA, 99%, CAS 5835-26-7), sandaracopimaric acid (SanA, 88%, CAS 471-74-9), were all purchased from Helix Biotech Scientific (Richmond, Canada). The oxidized resin acid 7-oxodehydroabietic acid (7-O-DeA, CAS 18684-55-4) was synthesized in house (Figure 1). The synthesis followed two steps, the first involving an optimized procedure from Fleck et al²⁶ and the entire synthesis has been described previously.²¹ Podocarpic acid (98%, CAS 5947-49-9) from Sigma Aldrich (Milwaukee, Wisconsin) was used as internal standard (IS).

Portuguese gum rosin (CAS 8050-09-7), that had been stored in a glass jar for more than 25 years, was also analyzed for comparison.

Stock solutions of derivatized reference compounds were prepared in acetone at a concentration of 200 $\mu\text{g/mL}$ of each compound and stored in freezer ($-25\text{ }^{\circ}\text{C}$) until use.

Working standard solutions for calibration were prepared at six different levels between 0.1 and 10 µg/mL. To evaluate LOD & LOQ, six different levels within the range 0.01 to 0.5 µg/mL were used in triplicate. A stock solution of IS in acetone was made at 50 µg/mL.

Solid-phase extraction (SPE) columns, Oasis® Max (6cc, 500mg, 60 µm particles, 80 Å pore size), were purchased from Waters (Dublin, Ireland). The stationary phase consists of a mixed-mode reversed-phase polymer, substituted with strong anion-exchanging quaternary amine functions.

2.2 Investigated consumer products

Consumer products were purchased from the Swedish market and from internet shops during the autumn of 2018. The products were selected based on prior experience from analyses of consumer products.^{5,6,16,21,24,25} Analyses of 15 different commercial products originating from varying countries were performed, including products from Sweden, Italy, France, Canada, Germany, China, Poland and United Kingdom, see Table 1. Four main types were investigated, including two shoe insoles, adhesives and surgical tapes, sticky glued papers (post-it-notes, roller for removal of hair and dust), and cosmetics (mascara, foundation and lipstick), respectively.

2.3 Sample preparation

Different amounts of samples were taken out for analysis, see Table 1. The extraction procedure including solvent ultrasonication followed by solid phase extraction (SPE) has been published previously²¹ and was slightly modified. Briefly, samples were weighed and then spiked with 5.0 µg of IS prior to ultrasonication in 30 mL of acetonitrile for 30 min. The samples were extracted once more using the same procedure but without addition of IS. The pooled extracts were evaporated under a gentle stream of nitrogen to approximately 5 mL. Thereafter, a volume of 5 mL of aqueous solvent was added (2 mL ACN + 3 mL water). In cases when an opaque solution was formed, samples were filtered through a 0.2 µm polypropylene syringe filter (Whatman) prior to the SPE clean-up step²¹. The resulting elution fraction from SPE was evaporated until dryness and then re-dissolved in toluene using ultrasonication prior to derivatization with PFBBBr in toluene. A previously described derivatization procedure was followed²³, but with 20%

(v/v) solution of PFBBr instead of 2%. After a reaction time of 1 h at 90°C, all studied resin acids were shown to be fully derivatized. After the derivatization, the sample was evaporated to dryness, reconstituted in 1 mL of acetonitrile, ultrasonicated and subjected to GC/MS.

For the analysis of the Portuguese gum rosin sample, a piece was ground, weighed and diluted with acetone and ultrasonicated until fully dissolved. An aliquot of 100 µL was taken out for analysis and spiked with 400 µL (20 µg) of IS. No clean-up step was applied on this sample and it was directly subjected to evaporation to dryness, derivatization and GC/MS using the same procedure as for the consumer products.

The recoveries from the SPE were tested for four of the resin acids. The amounts loaded on the SPE column for recovery test were 6.0 µg each of AbA, DeA, IsoA, and 7-O-DeA, while the amount of added IS was 5.0 µg. The yields varied between 88 and 95% (RSD 5-14%, N=5).

TABLE 1: Investigated consumer products

Sample	Country	Amount analyzed (mg)
Shoe insole 1 (safety shoes) [†]	Canada	1000
Shoe insole 2 (running shoes) [†]	China	1000
Adhesive 1 (woven) [‡]	Sweden	500
Adhesive 2 for kids (water-resistant) [‡]	UK	250
Adhesive 3 (water-resistant) [‡]	Sweden	250
Surgical tape 1 (woven) [‡]	Germany	500
Surgical tape 2 (woven) [‡]	Poland	500
Post-it-note [‡]	France	1000
Roller for dust removal [‡]	China	500
Gloss lipstick, fluid	Italy	1000
Cream lipstick 1 [§]	China	1000
Cream lipstick 2 [§]	Italy	1000
Matte lipstick, fluid	France	1000
Mascara, fluid	Italy	1000
Foundation, fluid	Italy	1000

[†] Pieces of 2x2mm were cut from a part of uniform thickness

[‡] Pieces of 3x3mm were cut from the sticky part

[§] Cut into smaller pieces

Neither of the products were labelled with risk phrases EUH208 or H317. Content of colophonium was labelled on lipstick 1 and 2. Lipstick 1 was labelled with the phrase “Colophonium is a component of this product. Discontinue use if irritation occurs”. No other products declared a content of colophonium or derivatives thereof to the best of our knowledge.

2.4 GC/MS analysis

A Varian 320-MS triple-quadrupole instrument equipped with a Varian 450-GC and a Varian PAL autosampler were used for the GC/MS analyses. The GC injector was operated with the temperature set to 250°C and in split-less mode for 2 min, and the injection volume was approximately 1 µL. The samples were separated on a DB-5 column from Agilent J&W Scientific (Santa Clara, California). The initial oven temperature in the GC program was set to 65°C for 2 min. The temperature was then increased by 30°C/min up to 200°C, followed by a gradient of 5°C/min up to 300°C. The final temperature was held for 10 min. The temperature of the transfer line to the MS was set to 280°C.

The MS analyses were run in electron ionization (EI) mode, with the electron energy and source temperature set to 70 eV and 178°C, respectively. For identification of the resin acids, the acquisition was performed with a full scan cycle of 200 - 700 m/z in 0.6 s. Quantification was performed in SIM mode with analyte-specific quantifier and qualifier ions, each with a dwell time of 55 ms. The monitored qualifier/quantifier ions for each resin acid were: AbA m/z 301/482; PalA m/z 467/482; NeoA m/z 301/482; DeA m/z 480/239; PimA m/z 467/482; IsoA m/z 482/241; SanA m/z 467/482; 7-O-DeA m/z 494/253; IS m/z 454/213.

3. Results

The extraction of resin acids from the tested consumer products was evaluated and found to be exhaustive. After extracting twice by ultrasonication, no resin acids could be detected in a third extract. However, it should be observed that the number of sample types in this study is limited and that it might be necessary to evaluate the extraction recoveries for other types of consumer products. The mixed-mode SPE yields a highly selective extraction of resin acids. For all examined consumer products, pure GC/MS chromatograms were obtained after clean-up and derivatization. The strong selectivity of the SPE is due to the interactions of resin acids with both anion-exchanging and lipophilic/aromatic functions of the stationary phase. The identified and quantified resin acids, including 7-O-DeA, corresponded to more than 90% of the peak areas. Only a few very minor peaks that could correspond to other resin acids were detected, but no attempt to identify these compounds were made. The instrumental limit of detection (S/N=3) in SIM mode varied between 0.3 and 12 pg injected on column and the responses were found to be linear up to the highest tested level, 10 ng injected.

3.1. Colophonium in consumer products

Resin acids were identified in nine of the 15 tested consumer products. In Table 2 are listed the levels of individual as well as the total of resin acids.

As shown in Table 2, the relative content of the individual resin acids varies extensively between the different products, with the highest total level detected in adhesive 1 made of woven fabric. The GC/MS chromatogram in Figure 2 illustrates the separation of the

PFBBBr-derivatized resin acids from this sample. AbA, DeA, and the pimaric-type resin acid IsoA each occurs in adhesive 1 at approximately one third of the total resin acid content, which was determined to 756 ppm (0.08%). These compounds were the most frequent together with 7-O-DeA, and found to be the major constituents in most, although not all samples. Apart from this, there is no clear pattern regarding the relative levels. For instance, PaA was detected at higher concentrations than AbA in both adhesive for kids and in the safety shoes (shoes 1). The ratio AbA/total resin acids in the different samples were shown to vary from 8% (w/w), as in the post-it notes, to about 50% in the water-resistant adhesive 2.

Table 2 shows the estimated content of colophonium in the investigated products based on a comprehensive quantification of all detected major resin acids also including 7-O-DeA (Σ RA). An estimated content of 10 % non-acid compounds, the neutral fraction (NF) is added (Σ RA+NF). In our previous work, colophonium content in technical products was estimated based on the assumption that AbA constitutes 30 % (w/w) of the major resin acids which constitute approx. 90 % of unmodified colophonium⁵. In Table 2 we also show the results from this strategy, but assuming that the sum of AbA and 7-O-DeA constitutes 30% of the resin acids (since AbA is the source of 7-O-DeA) and adding the estimated NF fraction 10 % (Estim Σ RA+NF). The estimation based on quantification of only AbA +7-O-AbA yielded approx. 50 % lower levels for 3 of 9 products (post-it notes, roller and safety shoe insole) as compared to the concentrations from quantification of all detected resin acids. For adhesive 3, this strategy gave approx. a 30-% lower level, while 50-60 % higher levels were obtained for adhesive 2 and lipstick 2. The results agreed for only three of the samples (adhesive 1, running shoe insole and lipstick 1).

Comparing the ratio 7-O-DeA/AbA for each product shows a variation from 1.4 % (Adhesive 2) to 74 % (post-it notes) (Table 2).

Table 2. Quantification in ppm[†] of individual resin acids (RA) and measured total RA (Σ RA) detected in nine of 15 consumer products. The neutral fraction (NF) is assumed to be 10% (w/w) of colophonium. Σ RA+NF is the total RA (measured) + NF. Estim Σ RA+NF is based on the assumption that Σ AbA+7-O-DeA constitute 30% (w/w) of colophonium. Σ RA+NF and Estim Σ RA+NF reflect different strategies to calculate the content of colophonium. Relative standard deviations (RSDs) were below 13% for all samples.

	Adhesive 1	Adhesive 2	Adhesive 3	Post-it	Roller	Shoe 1	Shoe 2	Lipstick 1	Lipstick 2
AbA	196.8	117.9	65.3	2.3	9.5	8.7	7.5	27.4	51.1
PalA	30.1	26.4	79.4	n.d.	1.0	15.8	0.7	n.d.	9.5
NeoA	n.d.	3.1	15.6	n.d.	0.5	3.7	n.d.	n.d.	n.d.
DeA	214.7	59.5	25.4	13.6	33.4	23.3	14.1	37.8	40.9
PimA	51.3	n.d.	53.1	n.d.	3.9	5.3	n.d.	7.6	6.0
IsoA	206.7	33.1	79.6	7.0	13.7	10.4	0.6	35.6	10.5
SanA	28.2	n.d.	15.5	2.8	2.9	4.5	n.d.	3.6	n.d.
7-O-DeA	27.7	1.6	9.7	1.7	0.8	1.3	1.1	16.3	7.7
Σ RA	755.5	241.6	343.6	27.4	65.7	73.0	24.0	128.3	125.7
Σ RA+NF	839.4	268.4	381.8	30.4	73.0	81.1	26.7	142.6	139.7
Estim Σ RA+NF	823.1	438.2	275.0	14.7	37.8	36.7	31.5	160.2	215.6
7-O-DeA/AbA	14%	1.4%	15%	74%	8.4%	15%	15%	59%	15%

[†]equal to $\mu\text{g/g}$

n.d. = not detected

Adhesive 1=woven fabric

Adhesive 2=water-resistant

Adhesive 3=water-resistant, for kids

Shoes 1=Safety shoe insole

Shoes 2=Running shoe insole

Lipstick 1= from China, labelled with the phrase "Colophonium is a component of this product. Discontinue use if irritation occurs"

Lipstick 2= from Italy

3.2. Resin acids in Portuguese gum rosin

The relative levels of resin acids and the oxidation product 7-O-DeA were quantified in triplicate in an old sample of Portuguese gum rosin, for comparison and validation. The results are shown in Table 3. For comparison, literature values are also given. Levopimaric acid is not included in the table. This is the most unstable of the abietadiene acids and often not detected in conventional analysis.

Table 3. Results from the quantification of individual resin acids (RA) and total of the studied resin acids (Σ RA) in an analyzed old Portuguese gum rosin sample, in comparison with literature values f.⁷ RSD= relative standard deviation. NA= Not analyzed

	Conc (mg/g)	RSD (%)	Conc (%)	Literature ⁷ (%)
AbA	177.8	18	18	48
PalA	9.1	14	1	15
NeoA	11.5	6	1	15
DeA	179.3	10	18	5
PimA	37.8	4	4	9
IsoA	39.2	7	4	5
SanA	26.7	4	3	2
7-O-DeA	31.5	3	3	NA
Σ RA	512.9		51	99 [†]

[†] 1% of other resin acids.

It can be seen from Table 3 that the old gum rosin sample had autoxidized extensively, as approx. 30 mg/g (3%, 30 000 ppm) of 7-O-Dea was detected, while the total level of identified resin acids was only 51%, in comparison with 100% for the corresponding reference values from the literature.⁷ It must be noted that the values presented exclude both the neutral fraction and other oxidation products than 7-O-DeA, and are thus largely dependent on the status of autoxidation. As can be seen, the concentrations of the most easily autoxidized abietane-type acids, AbA, PalA and NeoA have decreased while the concentration of the more stable DeA has increased in comparison with the reference values.

4. Discussion

For preventive purposes, an analytical method following the legislation is important. The present study shows that an estimation of the colophonium content based on quantification of solely AbA is not generally valid since there is no characteristic pattern in the relative levels of AbA. Instead, a comprehensive measurement of the major resin acids in unmodified colophonium with addition of a major stable oxidation product of AbA (7-O-DeA) is to be preferred. The analytical method used in this work is simple,

reproducible and fast, suitable for comprehensive screening purposes. It can also easily be transferred from GC/MS analysis to less expensive GC/FID analysis, as long as there are reference compounds available.

The concentrations were all $< 0.1\%$, but for one of the adhesives the colophonium level was close to this limit. For both lipstick 1 and 2 a content of colophonium was declared and lipstick 1 from China, was labelled with a warning "Colophonium is a component of this product. Discontinue use if irritation occurs". Although other products contained higher concentrations, no colophonium content was given nor was any warning found on these products. AbA and other abietic- type acids autoxidize at air exposure and form skin sensitizing oxidation products. It is important to be aware of that quantification of only AbA will often lead to an underestimation. Determination of the ratio 7-O-DeA/AbA is a way of keeping track on the autoxidation of colophonium which implies a higher risk of sensitization/elicitation. A low concentration of AbA might be due to extensive autoxidation. Interestingly, the ratio 7-O-DeA/AbA in lipstick 1 was found to be 59% indicating a higher degree of autoxidation and risk compared to lipstick 2 with a ratio of 15%. We suggest to include 7-O-DeA/AbA in the characterization of the colophonium quality used in consumer products. A high ratio indicates autoxidation and an increased risk of skin sensitization.

With regard to modified colophonium we cannot give any exact results but according to our experience no resin that could be associated with modified colophonium could be detected on the label of any of the 15 products.

It is difficult to trace and assess the exposure of the general population to chemicals that are ubiquitous in our environment and to which we are all constantly exposed. This is especially true for complex natural products added to consumer products. However, for a correct diagnosis of already sensitized individuals and to avoid elicitation of allergic contact dermatitis from colophonium allergens, it is important with analytical methods that can measure lower levels than the limit (0.1%). The obtained results show that colophonium is still common in the same type of consumer products as shown previously.

Colophonium is a well-known cause of shoe allergy in glues and finishes or as tackifier. The frequency of sensitization to colophonium in foot dermatitis patients was about twice as high as in the control group of patients with suspected contact sensitization to other allergen sources and comparable to earlier data according to a new retrospective study from the IVDK (Information Network of Departments of Dermatology).²⁷ It should be noted that colophonium in shoes is often modified by esterification or Diels-Alder reactions, whereby new strong sensitizers are formed that do not cross-react with the haptens in unmodified colophonium.^{15,25,28,29}

Since colophonium is a natural product, non-toxic and with very good adhesive properties, it finds usage when technical devices are fastened to the skin, such as insulin infusion sets. A case study showed that a young girl with diabetes, who got sensitized to colophonium due to the adhesive used to fasten her glucose sensor, developed vulvar eczematous reactions when she grew older and started to use sanitary pads.³⁰

5. Conclusions

For preventive purposes, a suggestion is to measure the colophonium content in consumer products as the sum of all detectable major resin acids from unmodified colophonium including 7-O-DeA, plus an assumed portion of neutral compounds of 10%. The ratio 7-O-DeA/AbA should be used as a marker of autoxidation. This will give an indication of the status of oxidation of AbA, which is important as a high content of oxidation products increases the risk of allergenic effects from the consumer products. The presented analytical method is simple to use and suitable for further in-depth studies.

Conflicts of Interest

None declared.

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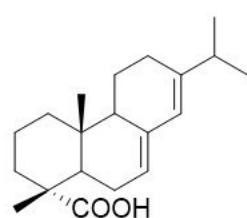
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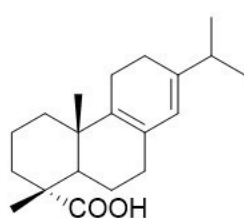
Figure legends

Figure 1. The major resin acids in unmodified colophonium and the marker of autoxidation, 7-oxodehydroabietic acid (7-O-DeA)

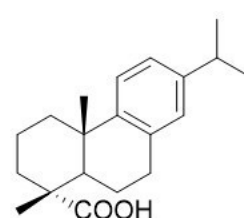
Figure 2. A gas chromatography/mass spectrometry (GC/MS) chromatogram of derivatized resin acids extracted from the adhesive of woven fabrics. The carboxylic acid function was esterified with 2,3,4,5,6-pentafluorobenzyl bromide (PFBBBr) prior to GC/MS analysis. PimA= Pimaric acid; SanA= sandaracopimaric acid; IsoA= isopimaric acid; PalA= palustric acid; DeA= dehydroabietic acid; AbA= abietic acid; IS (internal standard)= podocarpic acid; 7-O-DeA= 7-oxodehydroabietic acid; *= not identified.



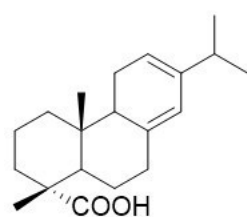
Abietic acid



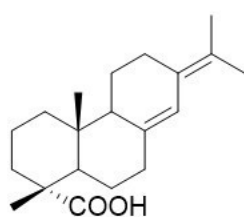
Palustric acid



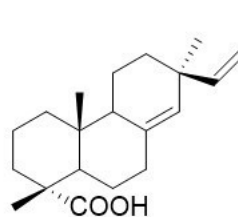
Dehydroabietic acid



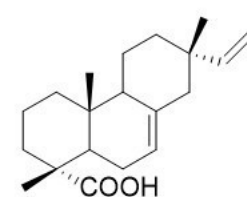
Levopimaric acid



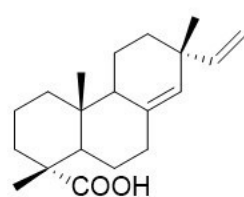
Neoabietic acid



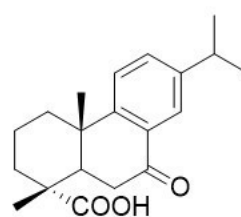
Pimaric acid



Isopimaric acid



Sandaracopimaric acid



7-Oxodehydroabietic acid

Figure 1 .jpg

Figure 2

