Headspace Constituents of Shellac

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Shellac CO_2-Extract, Headspace, GC-MS Spectra, GC-FTIR Spectra, GC-Sniffing-Technique

By headspace analysis of the CO_2-extract of shellac 4-methyl-3-penten-2-one (29.57%), 4-hydroxy-4-methyl-2-pentanone (16.66%) and 3-methyl-1-butanol (15.41%) could be identified as main constituents, as well as nearly forty hitherto unknown minor constituents (hydrocarbons, alcohols, aldehydes, ketones, acids and mainly C_4–C_8-esters). This investigation was carried out using GC-FID, GC-FTIR-MS and GC-Sniffing-Technique.

Introduction

Shellac as commercially used natural resin of animal origin (from the tiny insect Kerria Lacca) has gained greater importance in pharmacy, cosmetics, fragrance and food chemistry, especially for its non-toxicity [3, 4, 6–10]. The fragrance industry uses aleuritic acid (9,10,16-trihydroxyhexadecanoic acid) as valuable synthon for the synthesis of zivetone, ambrettolide and other olfactory lactones [6–8], as well as for the synthesis of some pheromones (especially used against flies in India [7, 8]).

The aim of this investigation was the identification of the main volatile odour components in the headspace of shellac extract (CO_2) using GC-MS and GC-FTIR in combination with the GC-Sniffing-Technique as well as the olfactoric evaluation to get information about the composition of the hitherto uncharacterized odour of this valuable natural product.

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Results and Discussion

The headspace of the shellac CO_2-extract was trapped by use of a commercial pumping and trapping system (closed loop stripping [1, 2, 5]), olfactorically evaluated and investigated by means of GC-FID, GC-MS, GC-FTIR and GC-Sniffing-Technique. The odour of the headspace sample was described by perfumers as weak tobaccolike, fruity, plumlike and in the background fatty.

As main constituents of the shellac headspace the two ketones 4-methyl-3-penten-2-one, 4-hydroxy-4-methyl-2-pentanone and the alcohol 3-methyl-1-butanol could be identified, but also some alcohols and two esters (concentration higher than 1%, see Table I) were found.

Table I. Main constituents of the headspace of Shellac CO_2-extract (peak area percentage of GC-FID measurement).

No.	Compound	Concentration (%)
1	4-Methyl-3-pentene-2-one	29.57
2	4-Hydroxy-4-methyl-2-pentanone	16.66
3	3-Methyl-1-butanol	15.41
4	1-Hexanol	4.16
5	1-Heptanol	4.03
6	Pentanoic acid ethyl ester	3.49
7	1-Nonanol	2.89
8	*n*-Butanol	2.14
9	1-Pentanol	1.94
10	Decanoic acid ethyl ester	1.68

As minor constituents of the headspace sample (concentration less than 1%) more than thirty compounds were detected and identified by GC-FID (retention time correlation) and GC-FTIR-MS (mass spectra and IR spectra correlation) analyses (see Table II).

Applying the GC-Sniffing-Technique on this shellac extract the following characteristics could be found: Solvent odour in the range of propanoic and butanoic compounds, shellac-like odour in the range of pentanoic compounds and weaker near nonanoic compounds, fruity (especially gooseberrylike) and green odour in the range of hexanoic and heptanoic compounds, weak tobaccolike, smoky and fatty odour in the range of decanoic to octadecanoic compounds. These olfactoric results are in very good agreement with the olfactoric evaluation of the total headspace sample of shellac-CO_2-extract.

Table II. Minor constituents of the headspace of shellac CO_2-extract (in alphabetical order).

No.	Compound
1	Acetic acid isopentyl ester
2	Acetic acid 1-phenylethyl ester
3	Adipic acid dimethyl ester
4	Butanoic acid ethyl ester
5	1-Butanone
6	1,8-Cineole
7	Decanoic acid methyl ester
8	1,1-Dimethoxy-2-propanone
9	3,5-Dimethyl-2-cyclohexen-1-one
10	1-Ethyl-cyclohexane
11	2-Furaldehyde
12	Heptanoic acid ethyl ester
13	2-Heptanone
14	Hexanoic acid ethyl ester
15	Hexyl cinnamaldehyde
16	4-Hydroxy-butyric acid-γ-lactone
17	1-Methyl-cyclopentane
18	3-Methyl-1-pentanone
19	Nonanoic acid ethyl ester
20	2-Nonanone
21	Octanoic acid ethyl ester
22	2-Octanone
23	1-Octen-3-ol
24	2-Octyne
25	Oleic acid methyl ester
26	Palmitic acid ethyl ester
27	Propanoic acid ethyl ester
28	*n*-Propanol
29	1-Phenylethanol
30	Undecanoic acid ethyl ester
31	1-Undecanol
32	Undecane-2-one

Experimental

The CO_2-extract (SFC-method) of shellac resin (from India), a pale yellow liquid with a white residue, was obtained from MHP Shellac Comp. (Hamburg, Germany).

Headspace: Pumping and trapping system G 24/02 from H. Brey Comp. (Germany) with absorption charcoal tubes Lot 120 Niosh (SKC Inc., USA). Trapping time: 65 h (closed loop stripping) and desorption with 200 μl of dichloromethane.

GC: A 14A GC with integrator system from Shimadzu Comp. (Japan), 30 m RSL-FSOT fused silica column (0.32 mm i.d. and 0.25 micron film thickness) from Biorad Comp. (The Netherlands). Temperature-programme: 40 °C/5 min to 280 °C with heating rate of 4 °C/min, injector temp.: 250 °C, detector: (FID): 300 °C, carrier gas: hydrogen, splitless mode, injected volume: 1.0 μl.

GC-FTIR-MS: An HP-5890A GC, an HP-5965B Infrared Detector (IRD, MCT detector) and an HP-5970B Mass Selective Detector (MSD) with the data systems HP-9000/340 (IRD) and HP-9000/300 (MSD) from Hewlett-Packard Comp. (USA). IR-range: 4000–850 cm^{-1}, MS-range: 40–450 amu (EI, 70 eV), carrier gas: helium, IRD cooling: liquid nitrogen, interface heating: 220 °C. Other parameters see GC-part.

GC-Sniffing-Technique: A Fractovap-2101 GC with LT-Programmer 230 and Electrometer-160 (Carlo Erba Comp., Italy). Column: 30 m RSL-FSOT mega bore fused silica column (0.53 mm i.d. and 1.0 micron film thickness; Biorad Comp., The Netherlands), carrier gas: hydrogen, sniffing capillary heating: 250 °C, split-ratio (FID/nose) 1:50. Other parameters see GC-part.

Olfactoric evaluation: 5 μl of the headspace dichloromethane sample was placed on a commercial odour strip (Dragoco Comp., Germany) and evaluated by fragrance chemists and a perfumer.

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