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Gas chromatography–mass spectrometric analysis of products from on-line pyrolysis/silylation of plant gums used as binding media

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ABSTRACT

Plant gums are complex polysaccharides used in the field of cultural heritage especially as binding media. Classification of polysaccharides may be achieved on the basis of monosaccharides composition after cleavage of glycosidic bond. Characterization of plant gums in works of art is complicated by the necessity of to use a method minimally invasive and requiring a small mount of sample.

Pyrolisys is an useful method to obtain polysaccharides decomposition and generally pyrolysis products can be identified by the use of gas chromatography–mass spectrometry. This paper describes a method where two plant gums, arabic and tragacanth, were pyrolized in presence of silylating agents (HMDS e BSTFA alone and with TMCS as catalyst) using an on-line Py-GC/MS apparatus. Some characteristic trimethylsilyl derivatives of monosaccharides were identified on the basis of mass spectra. The presence of characteristic pyrolysis products of sugars allows to distinguish the two gums.

1. Introduction

In the field of conservation and restoration it is important to know the exact nature of the materials used by artists in the past. Binding media for paints were obtained from various sources and applied according to artistic traditions and the desired aesthetic characteristics. Materials were traditionally obtained from natural sources, and binders and dyes in particular were often derived from plants.

Plant gums have been used since the most ancient time as coatings or binding agents for water based paints, particularly on cellulosic support such as paper. They have been found on decoration of *cartonnage*, a material used in the Ancient Egypt for funerary masks manufacture [1], and in the Middle Age they were widely employed [2] for illuminated manuscripts and for mosaic gold. At present, plant gums are the binders of modern tempera and watercolour paintings.

Plant gums are complex polysaccharides obtained from a variety of different vegetables. The plant gums more widely employed as paint media were gum arabic, gum tragacanth and fruit tree gum. Gum arabic exuded from *Acacia senegal* and *Acacia seyal,* common in the territories of Senegal, Red Sea, India, Pakistan and Iran. Gum tragacanth comes from Astragalus (Turkey, Kurdistan and Persia) [3] and fruit tree gums are obtained mainly from cherry trees. The polysaccharides contained in the gums comprise various units of sugars (aldohexoses and aldopentoses) and uronic acids. The complex nature of polysaccharides makes their precise characterization difficult. In the literature several descriptions of the gum arabic composition may be found and the simpler gives only a list of the monosaccharides obtained from chemical hydrolysis of the polysaccharidic structure [4–7]. More detailed models suggest a structure based on D-galactopyranose monomers bonded by 1-4 and 1-6 linkages. Connected to the main polymer chain there are branches formed by D-galactopyranose units and D-glucuronic acid monomers and other chains composed of L-arabinofuranose and L-rhamnopyranose [8]. In another model it is proposed that the base molecule of gum arabic is arabinogalactan (AG), an arabinose and galactose copolymer, while rhamnose, glucuronic acid or methyl glucuronic acid units are found as side chains. One study also proposed that gum arabic structure contains arabinogalactan units on a proteic skeleton [9–11].

Gum tragacanth is formed by polymer chains whose main components are L-arabinose, D-xylose, L-fucose and D-galacturonic acid units, with glucose, rhamnose, glucuronic acid and galactose present as minor components [5–7].

The analysis of plant gums is complicated by the necessity of preliminary scission of polymeric chain in order to obtain the constituent monosaccharides or other characteristic marker compounds. Since the aim of this study is the characterization of materials from works of art, the analytical method must be as much as possible minimally invasive. Conventional approach to obtain polysaccharide decomposition is the chemi-

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cal hydrolysis (for example microwave assisted acid hydrolysis), followed by GC or LC analysis [7,6]. Another useful method is methanolysis, that permits the best recovery of aldose and uronic acids [4,12]. Chemical hydrolysis and methanolysis are efficient but more expensive in terms of time, reagents and sample consumption.

Analytical pyrolysis with on-line derivatization is a method that requires a small amount of sample and no preliminary treatments, but only the addition of a reagent prior to pyrolysis. Derivatization is necessary because the presence of hydroxyl groups gives rise to excessive interactions in the chromatographic column, with peak broadening and loss of resolution [1,4,13]. Therefore OH groups must be converted into methylated or silylated derivatives.

Methylation is often performed with tetramethylammonium hydroxide (TMAH), however, it occurs with partial loss of structural information [14,15]. In fact the basic reagent also induces alkaline hydrolysis in the monosaccharides, giving rise to aldonic acids with one —OH group less than in the starting sugar molecule. The —OH group in position 2 is involved in hydrolysis, thus epimer sugars give the same derivatization product and therefore cannot be distinguished [14]. Trimethylsilyl derivatives, on the other hand, do not suffer from this problem, and furthermore they are more thermally stable and volatile than the corresponding underivatized precursors.

Very few studies have been described on the pyrolysis/silylation of carbohydrate molecules, and more particularly we have found no references on the application to plant gum characterization. Pyrolysis/silylation with hexamethyldisilazane (HMDS) has been applied on monosaccharides and on cellulose [16,17] while analysis of lignin has been performed with *N*,*O*-bistrimethylsilyltrifluoroacetamide (BSTFA) [18]. Recently, we have investigated the analytical pyrolysis of neutral sugars and uronic acids without derivatization and in the presence of HMDS or of BSTFA alone and with addition of trimethylchlorosilane (TMCS), and the different efficiency of the derivatization methods has been discussed [19]. Based on those previous results, we have studied the application of the different silylation methods to the analysis of gum arabic and gum tragacanth, with the aim of developing a simple and rapid method to characterize plant gums used as pictorial bindings, and the results are here described.

2. Experimental

Gum arabic in powder and gum tragacanth in flakes were purchased from Phase Prodotti per il Restauro (Florence, Italy) and used in this study without any purification treatment. Watercolour samples in tablets were supplied by Maimeri (Milan, Italy). Five different colours were used, containing different pigment: iron oxide (yellow ochre, no. 131), phthalocyanine beta (primary blue, no. 400), sodium polysulphide–alluminosilicate (ultramarine deep, no. 392), benzimidazolone (permanent orange no. 119) and chlorurated phthalocyanine (phtalo green no. 321).

The silylating reagents used were hexamethyldisilazane (HMDS), *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and mixtures of HMDS/TMCS and BSTFA/TMCS. The mixtures were prepared at the moment of the analysis by mixing 100 μg of HMDS or BSTFA with 15 μl of TMCS. All the reagents were obtained from Sigma–Aldrich.

The sample to be analysed (approximately 0.1 mg) was loaded into a quartz tube containing quartz wool, then inserted into the probe directly interfaced to the GC/MS apparatus and pyrolized using a CDS Pyroprobe 1000 (Analytical, Inc., USA) filament pyrolyzer.

GC analyses were performed with a 6890N Network GC System (Agilent Technologies, USA) gas chromatograph with a HP-5MS cross-linked 5% Ph Me Silicone (30 m, 0.25 mm i.d., 0.25 μm film thickness) capillary column. The program used was: 50 °C for 2 min, then a programmed temperature ramp to 300 °C (heating rate 10 °C/min to 130 °C, then 5 °C/min to 300 °C, held for 5 min). The carrier gas was helium (1.0 ml/min) and split ratio was 1/20 of the total flow.

The mass spectrometer coupled to the GC apparatus was a 5973 Network Mass Selective Detector (Agilent Technologies, USA) with an electron impact ion source (70 eV) and a quadrupole mass analyzer.

All instruments were controlled by Enhanced Chem Station (ver. 9.00.00.38) software. The mass spectra assignments were done with the Wiley 138 and NIST1992 libraries.

The conditions for on-line pyrolysis without derivatization were the following: 10 s at 600 °C. The temperature of the injector and of the Py–GC interface was kept at 280 °C. Blank analyses were performed after each run, with the same instrumental parameters.

For the on-line pyrolysis/silylation the small amount of gum sample was placed in the quartz tube, then 5 μl of the derivatization reagent was added to the solid. The GC injector was kept at 280 °C and the pyrolysis temperature and time were set at 600 °C and 10 s, respectively. The Py–GC interface temperature was 280 °C in the presence of BSTFA and of the BSTFA/TMCS mixtures, and it was decreased to 150 °C in the presence of HMDS and of the HMDS/TMCS mixtures, to avoid fast volatilisation of HMDS, whose boiling point is 125 °C. In particular, it was observed that when HMDS or HMDS/TMCS was used there was a memory effect and more blank cleaning runs were required between the analyses. Memory effect is due to sample condensation in Py–GC interface when a lower temperature (150 °C instead of 280 °C) was set.

3. Results and discussion

3.1. On-line pyrolysis

In Fig. 1 are shown the pyrograms of the two gums obtained without derivatization and the main peaks are listed in Table 1. Both pyrograms may be divided in two parts: in the first one at lower elution times (0–10 min) pyrolysis products common to both gums are present, whereas in the second part at higher retention times characteristic products of different monosaccharides are detected.

Within the first group of products the furancarboxyaldehydes, which can be considered characteristic markers of aldose sugars in the pyrolysis of carbohydrates [20–22], were recognized. They are probably formed by ring opening, as already proposed in our previous study [19]. The only major difference in relation to the analysis of monosaccharides is that 5-hydroxymethyl-2-furancarboxyaldehydes are absent probably because the C-6 atom of hexose monosaccharides in gums are involved in glycosidic bonds, and OH group on this atom perhaps disappear after bond cleavage.

In the second part of the pyrograms some differences are evident. In gum arabic, in particular, pyrolysis products deriving from arabinose (peak 9) and galactose units (peak 12) are present [19]. In tragacanth gum markers of glucose (peak 13), arabinose (peak 9) and xilose (peak 11) were identified. Peaks 12 and 13 are anhydrosugars formed by pyrolytic reactions of galactose and glucose, and peak 9 and 11 are probably anhydrosugars derived from arabinose and galactose.

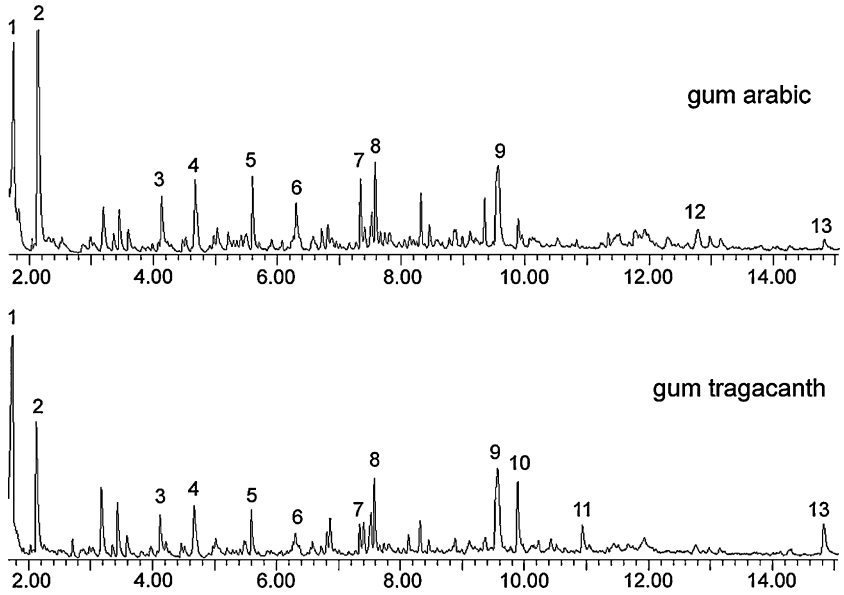

Fig. 1. Pyrograms of the gum arabic and gum tragacanth obtained without derivatization.

3.2. On-line pyrolysis/silylation with HMDS

In the pyrograms (data not shown) obtained from on-line silylation of the gums with HMDS neither furancarboxyaldehydes nor silylated sugars or anhydrosugars were present. Only bis-TMS-oxycyclopentenone and 3-TMS-oxy-2-TMS-oxymethyl-2-cyclopenten-1-one could be easily identified as two intense peaks, not well resolved, at retention times around 14.30 min. The mass spectra of other peaks showed typical fragment ions of trimethylsilyl groups. It is likely that the harsh pyrolysis conditions in the presence of the derivatization agent cause not only the breakage of the polysaccharidic structure, but also a more severe degradation of the monosaccharide fragments and of other marker compounds. Derivatization reactions may occur prior to glycosidic bond pyrolysis and the TMS groups further assist polysaccharides decomposition with formation of fragments whose structures are completely different from those of the monosaccharides contained in the polymer. Some of these particular fragments are the cyclopentenones, also considered characteristic compound obtained by carbohydrate pyrolysis [22,23]. The formation of cyclopentenones may occur after silylation of the polymeric structure. As cyclopentenones were observed in low concentration in pyrolysis carried out without derivatization, we may assume that their formation is favoured by silylation. The presence of both underivatized and derivatized products further indicates that pyrolytic cleavage and derivatization of hydroxyl groups are in competition.

The mechanism involved in the pyrolysis/silylation with HMDS of gums cannot be clearly established, and the method appears not suitable for gum characterization.

3.3. On-line pyrolysis/silylation with HMDS/TMCS

The on-line trimethylsilylation was also performed by adding TMCS to HDMS. TMCS is used to increase the silylation power of HDMS, a property attributable to the Cl atom which is a good leaving group in the nucleophilic derivatization process. Addition of TMCS greatly improved the results, making it possible to distinguish all the sugar molecules unequivocally through their pertrimethylsilyl derivatives [24,25]. In Figs. 2 and 3 the pyrograms obtained from gum arabic and gum tragacanth are shown. Main peaks are listed in Table 2 with the most significant *m*/*z* values.

The mass spectra of the peaks labelled with a letter are not those of sugars and anhydrosugars and are unidentified; however, we have previously found that these fragments are also present in standard sugar pyrograms and therefore they may be used as markers of the monosaccharides in the gum samples. All these unidentified mass spectra show the presence of typical fragments ions containing trimethylsilyl groups: *m*/*z* 73 $Si^{+}(CH_3)_3$;

Table 1
Characteristic pyrolysis products of gums without derivatization

Peak no.	Rt (min)	Assignment	Gum arabic	Gum tragacanth
1	1.73	Acetic acid	●	●
2	2.12	1-Hydroxy-2-propanone	●	●
3	4.17	2-Furancarboxaldehyde	●	●
4	4.67	1-Acetyloxy-2-propanone	●	●
5	5.60	5-Methyl-2(3H)-furanone	●	●
6	6.30	5-Methyl-2-furancarboxaldehyde	●	●
7	7.34	2-Hydroxy-3-methyl-2-cyclopenten-1-one	●	●
8	7.59	43, 58, 69, 87, 113, 128	●	●
9	9.57	43, 57, 60, 73, 86	●	●
10	9.89	43, 60, 71, 85		●
11	10.93	43, 57, 60, 73, 86		●
12	12.78	1,6-Anhydrogalactopyranose	●	
13	14.83	1,6-Anhydroglucopyranose (levoglucosan)	●	●

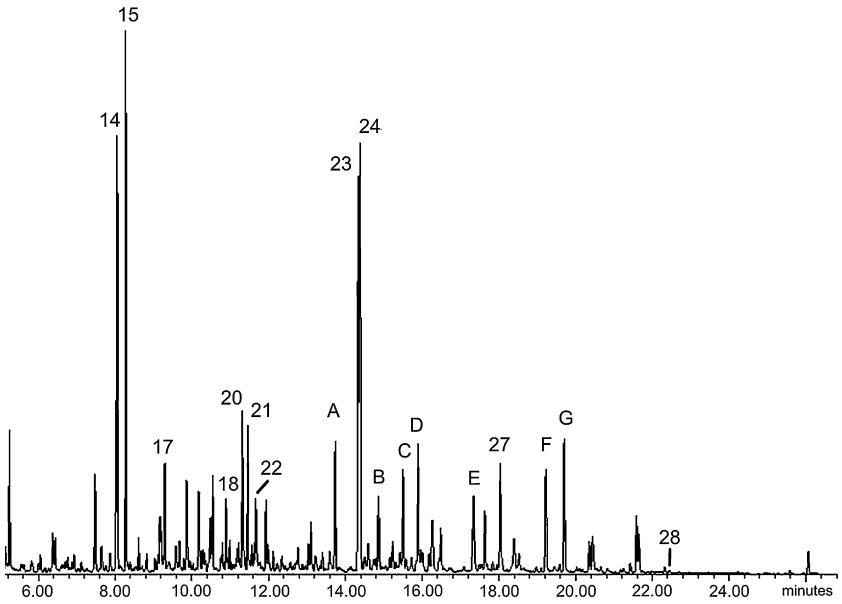

Fig. 2. Pyrogram of gum arabic obtained with on-line silylation with HMDS/TMCS.

m/z 103 $CH_2{=}O^+Si(CH_3)_3$; m/z 117 $O{=}CHCH_2OSi^+(CH_3)_2$; m/z 129 $(CH_3)_3SiC^+HCH{=}CH_2$; m/z 147 $(CH_3)_3SiOSi^+(CH_3)_2$.

In gum arabic some peaks coming from pyrolysis products of arabinose (peaks A, 27) and galactose (peaks B, E–G) were found. Glucuronic acid was present in the form of lactone, with a low intensity peak (number 28). Peaks denoting the presence of rhamnose were absent, even if this sugar is known to be present in the gum composition. Low amounts of glucuronic acid and absence of rhamnose markers are in agreement with the reported composition of gum arabic whose main constituents are arabinose and galactose. The percentages of other monosaccharides are very low, and they will not be visible in the pyrograms.

In the pyrogram of gum tragacanth peaks assignable to galactose (peaks B and G), arabinose (peaks A and 27) and glucose (peaks 25 and 26) were present. The latter compound was identified from two monosilylated isomers of levoglucosan. Other monosaccharides constitutive of gum tragacanth were not detected.

With HMDS/TMCS some of the main sugars present in the gums were identifiable and it is possible to distinguish gum arabic to gum tragacanth.

3.4. On-line pyrolysis/silylation with BSTFA/TMCS

BSTFA alone was not used because in our previous study it showed poor efficiency in silylating monosaccharides [19]. Therefore for polysaccharide characterization BSTFA has been used mixed with TMCS as catalyst.

With BSTFA/TMCS it was possible to identify anhydrosugars of galactose in the gum arabic pyrogram, while in gum tragacanth two mono-trimethysilylated isomers of levoglucosan were found. In both gums peaks B and G (data not shown), which are considered markers of galactose, were present. In gum arabic one peak with mass spectrum assignable to pertrimethylsilylated arabinose was also present. Both gums showed as common pyrolysis products

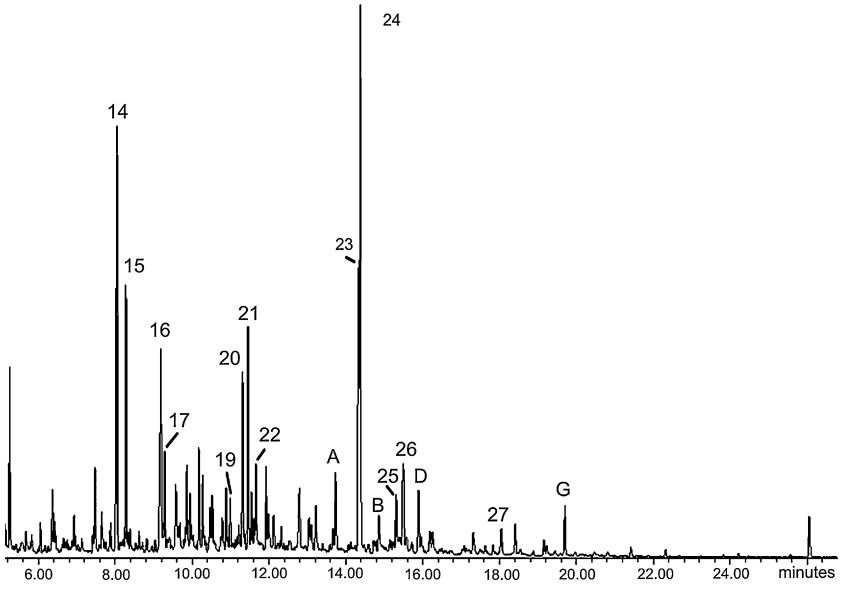

Fig. 3. Pyrogram of gum tragacanth obtained with on-line silylation with HMDS/TMCS.

Table 2
Pyrolysis/silylation product of gums with use of mixture HMDS/TMCS

Peak no.	Rt (min)	Assignment
14	8.05	2-(*O*-TMS)-Propanoic acid, trimethylsilyl ester
15	8.28	Hydroxyacetic acid trimethylsilyl ester
16	9.18	73, 152, 167
17	9.29	3-(*O*-TMS)-2-Furaldehyde
18	10.88	73, 75, 185, 200
19	10.99	73, 217, 232
20	11.32	73, 75, 101, 117, 129, 143, 158
21	11.46	Glicerol trimethylsilyl ester
22	11.66	73, 231, 246
A	13.73	73, 103, 129, 147, 217, 230
23	14.34	3-(*O*-TMS)-2-(*O*-TMS)-2-Cyclopenten-1-one
24	14.34	bis-TMS-oxycyclopentenone
B	14.86	73, 116, 255, 270
25	15.31	1,6-Anhydro-2(*O*-TMS)-glucopyranose
26	15.32	1,6-Anhydro-4(*O*-TMS)-glucopyranose
C	15.51	73, 103, 117, 129, 143, 147, 233
D	15.89	73, 103, 117, 129, 143, 147, 233
E	17.35	73, 103, 129, 145, 157, 170, 230
27	18.04	1,2,3,5-Tetrakis(*O*-TMS)-arabinofuranose
F	19.23	73, 103, 117, 129, 157, 191, 217, 243, 332
G	19.70	73, 103, 147, 255, 330, 345, 360
28	22.35	Per(*O*-TMS)-glucufuranurono-6,3-lactone

the cyclopentenones, also identified with the other silylation methods.

This derivatization method allowed the identification of some monosaccharide markers, but it cannot be recommended for precise characterisation of gums as the characteristic peaks are in general weak and assignment often uncertain. In the analysis of a complex sample, or of a mixture containing more than one gum, precise identification would be difficult, and it may only be possible to establish that some carbohydrate compound is present.

3.5. A case study: analysis of watercolour samples

As the HMDS/TMCS mixture resulted the best performing derivatization method, a selection of commercial watercolour samples has been analyzed with such mixture.

Watercolours were analyzed without any preliminary preparation or artificial aging. Being a solid tablet a small piece (approximately 0.1 mg) of colour were cut and inserted in a quartz tube and derivatizant was added with syringe.

Five different colours were tested, and all showed similar results indicating that the same binder was present. The presence of pigment was not detected and their presence does not significantly influence pyrograms profile, therefore only one sample is presented.

In Fig. 4, the pyrogram obtained from the orange watercolour is presented.

The intense peaks eluting between 8 and 12 min were present in all pyrograms; one of them was identified as trimethylsilylated glycerol, which may be attributed to the use of the polyhydric alcohol as plasticizer added during preparation of watercolours.

In the portion of the pyrogram eluting after 12 min it was possible to find a group of peaks that showed good overlap with the reference gum arabic pyrogram. Also, mass spectra analysis confirmed that the peaks were the same present in gum arabic.

In the colour samples two new peaks (F1 and F2) were also found. These peaks were assignable to pertrimethylsilylated sugars, even if they are not found in gum arabic and in monosaccharide samples. A tentative explanation for the presence of these peaks is that the gums used in colour preparation, coming from different sources than those of the standard samples, could contain different monosaccharides or monosaccharides linked in a different way in the polymer chains.

From the good matching between the pyrograms of gum arabic and the watercolours it is possible to establish the nature of these colours, and the analytical pyrolysis/silylation method which was

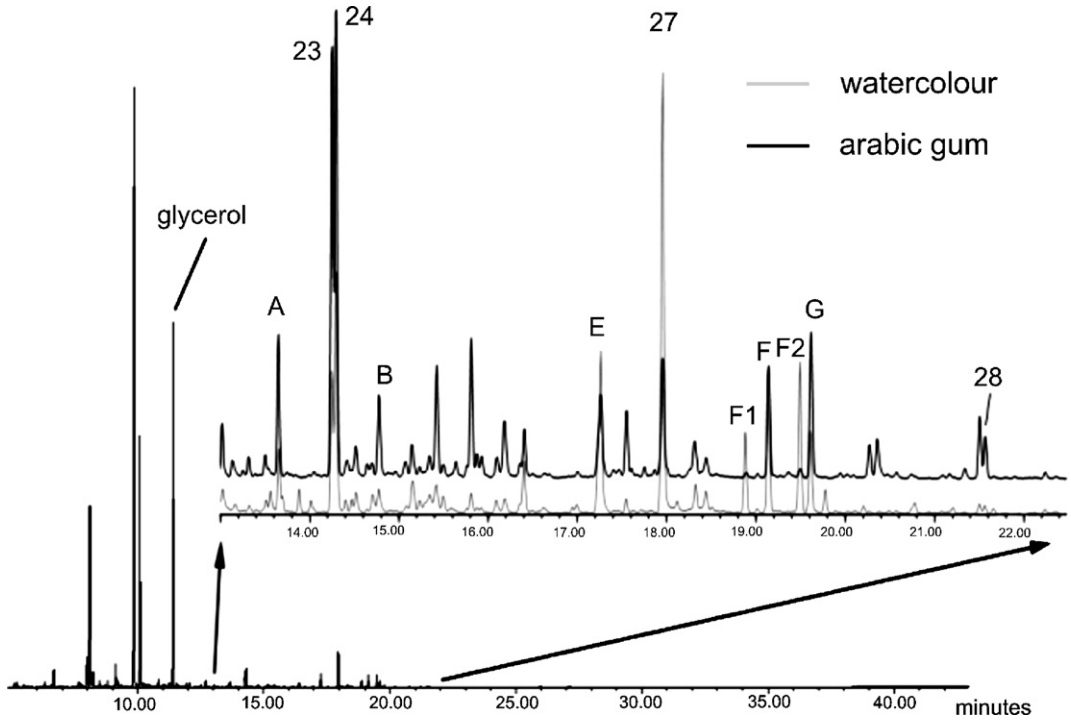

Fig. 4. Pyrogram of permanent orange watercolour sample (Maimeri, Milan, Italy).

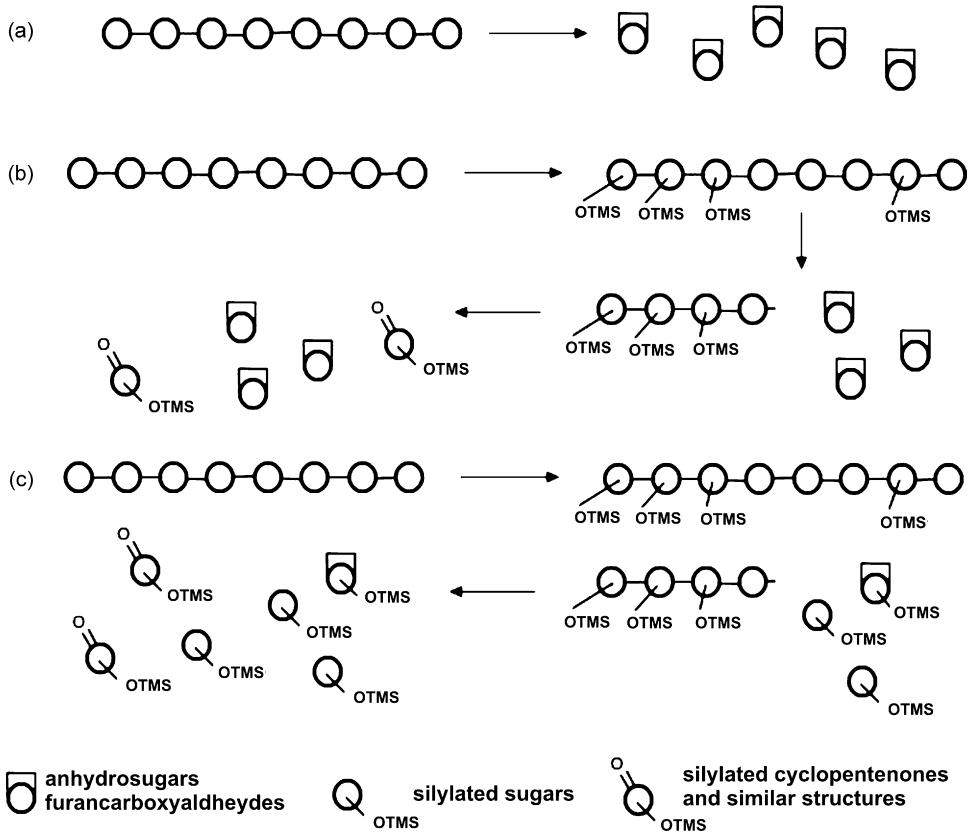

Fig. 5. Schematic representation of the product formation pathways with different method: (a) pyrolysis without derivatization; (b) pyrolysis with HMDS and BSTFA/TMCS; (c) pyrolysis with HMDS/TMCS.

developed appears to be suitable for fast recognition of plant gum binders in real samples.

4. Discussion

Pyrolysis without derivatization gives anhydrosugars and related molecules, furancarboxyaldehydes and smaller fragments, like hydroxyacetic acid. Silylation reactions with HMDS and BSTFA turned out to be incomplete even when aided with TMCS catalyst, as confirmed by the simultaneous presence of partially derivatized and underivatized products. Silylation was more efficient with the combined use of HMDS and TMCS, where the major part of the functional groups were silylated.

In the different methods investigated three types of reactions may be identified, each one characterized by specific products: (1) pyrolysis without derivatization, with formation of anhydrosugars and furancarboxyaldehydes; (2) low efficiency pyrolysis/silylation, such as with HMDS or BSTFA/TCMS, with formation of silylated cyclopentenones and partially derivatized molecules; (3) efficient pyrolysis/silylation, like in the HMDS/TMCS method, where the sugar markers and their fragments are present predominantly in the pertrimethylsilylated form. The product formation pathways may be summarized with the schemes shown in Fig. 5.

In the first pathway the pyrolysis of the polymeric gum produces anhydrosugars and furancarboxyaldehydes (Fig. 5a). In the second process the derivatization agents react partially with polysaccharides. From the underivatized part of the polymer monosaccharides are released, which under pyrolytic conditions become anhydrosugars and furancarboxyaldehydes. Silylated cyclopentenones are obtained from the silylated gum fragments (Fig. 5b). In the third mechanism (Fig. 5c) partial derivatization of the polymer and the simultaneous release of monosaccharides occurs. The greater efficiency of the HMDS/TMCS mixture allows silylation of the free monosaccharides [26] contained in the gum before they react to form anhydrosugars and furancarboxyaldehydes. In fact the latter compounds are found in low concentration and in silylated form. The remaining part of silylated chain gives the silylated cyclopentenones.

5. Conclusions

All the derivatization methods described in this work showed that in pyrolysis of plant gums characteristic markers of polysaccharides are formed, the more important ones being pertrimethylsilylated sugars, anhydrosugars, furancarboxyaldehydes and cyclopentenones.

Direct pyrolysis without derivatization allows a general characterization of polysaccarides, but the presence of OH group gives rise to retention and coelution of pyrolitic fragments. Products with similar retention time produce superimposed mass spectra, making difficult their identification. Therefore in real multicomponent samples it is likely that simple pyrolysis without derivatization will prevent the recognition of characteristic markers.

On the other hand, with proper derivatization methods pyrolysis products are well resolved and mass spectra more easily identifiable. It was possible to establish that the mixture HMDS/TMCS gives good diagnostic results, allowing differentiation of gum arabic and tragacanth and the identification of gum arabic in watercolour samples. However, also with this method some products are underivatized and different molecules are eluted together giving mixed mass spectra. The impossibility of identifying minor pyrolysis products may hinder accurate classification of plant gums, especially

in a complex sample or in mixtures of different carbohydrate materials.

Therefore it is desirable to further improve these characterization methods by modifying the experimental conditions in order to obtain best component separation and identification. Analysis of other gums from several suppliers should be done to consider variability in composition due to different origin of plants.

Pyrolysis/silylation is a useful method because only small amounts of sample are required and analyses are quite rapid. Optimization of the pyrolysis/silylation reactions will allow to obtain good results for real samples extracted from works of art.

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