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LETTERS

Cis-1,4-poly-β-myrcene; the Structure of the Polymeric Fraction of Mastic Resin (*Pistacia lentiscus* L.) Elucidated

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Abstract: The polymer fraction of mastic resin from *Pistacia lentiscus* L. was isolated and purified by extraction and Size Exclusion Chromatography. The molecular weight distribution of the polymer was broad and stretched up to 100,000 Da. The structure was characterised as 1,4-poly-β-myrcene, predominantly present in the *cis*-conformation. The compound is the first known example of a naturally occurring polymer of a monoterpene.

Mastic, or gum mastic, is a bleed resin formed in teardrops from the *Pistacia lentiscus* L. tree from the *Anacardiaceae* family. It has been known and was extensively traded in antiquity around the Mediterranean as adhesive, coating, medicine etc.[1-3] The best known international application in the last couple of centuries is the use as a spirit varnish for furniture and paintings.[3,4] Other species of the *Pistacia* genus which produce resin are *P. terebinthus* L. which produces a turpentine and *P. atlantica* Desf. which brings forth a mastic of inferior quality.[3]

Gum mastic consists of large amounts of triterpenoid molecules which have been studied in varying detail by a number of research groups.[2,5-12] The resin also contains a considerable amount of polymeric material of which the structure was not known before. In this letter, we describe the experiments for the elucidation of this polymeric fraction and present its chemical structure.

The polymer fraction of gum mastic teardrops (Schmincke, Erkrath, Germany) was isolated by dissolution with dichloromethane and precipitation with methanol[13] which was monitored using Size Exclusion Chromatography (SEC, absorption at 240 nm). The polymer fraction was found to have a molecular weight distribution up to about 100,000 Da (Fig 1). Polymeric material of 20,000-100,000 Da was collected using preparative SEC for further study.

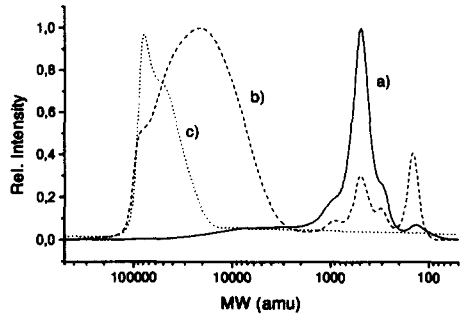

Figure 1. Size exclusion chromatograms of a) mastic, b) the polymer fraction after several dissolution/precipitation steps, c) the isolated polymer with SEC.

Direct Temperature-resolved MS (DTMS) after isobutane chemical ionisation (CI)[14] showed a low amount of monomeric material (triterpenoid molecules) still present, which desorbed at temperatures below 350 °C. Pyrolysis occurs at temperatures above 400 °C. The corresponding CI mass spectrum predominantly shows $[M+H]^+$ ions with an increment of 136 Da, indicating that the polymer consists of monomer units of 136 Da (Fig. 2). Oligomer fractions up to the 14-mer, with a nominal mass of 1904 Da (m/z 1906 due to ^{13}C contribution), are visible in the spectrum.

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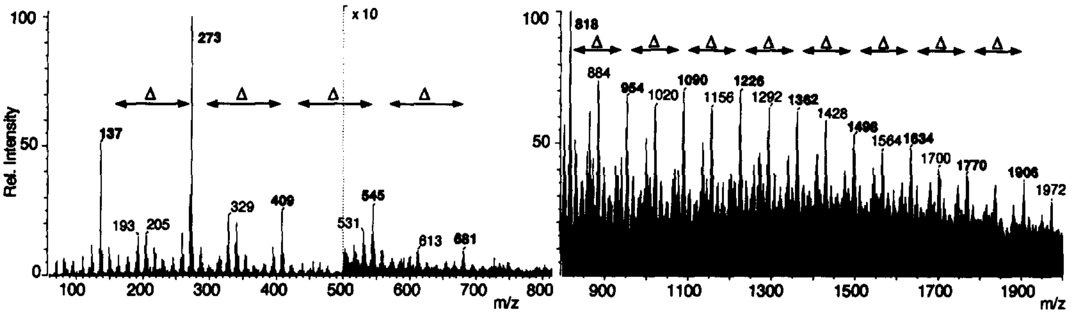


Figure 2. Mass spectra of the pyrolysate (>400 °C) of the isolated polymer of gum mastic, m/z 60-800 (a) and m/z 800-2000 (b). Δ = 136 Da (see text).

Curie-point pyrolysis GCMS (Cu-Py-GCMS, Cu-point 610 °C)[15] showed a large number of products, the most abundant of which are hydrocarbons C_xH_y (Fig. 3). The most abundant species was identified as β-myrcene ($C_{10}H_{16}$, 136 Da) which points towards β-myrcene as the monomeric base unit of the polymer. Several dimeric structures ($C_{20}H_{32}$) were found as well but the structure of these compounds could not be identified unequivocally. In addition, also some oxygen-containing molecules are present in the pyrolysate which may have been formed from low molecular weight impurities as well (*vide infra*).

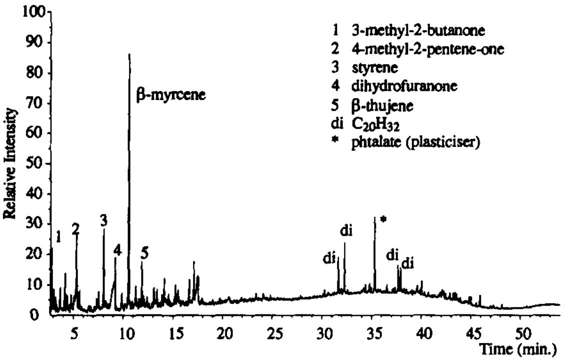


Figure 3. Py-GCMS total ion chromatogram of the polymer fraction of gum mastic.

FT-IR, ^{1}H-NMR (not shown) and ^{13}C-NMR data (Fig. 4) point to a hydrocarbon such as latex and gutta percha, natural rubbers that consist of 1,4-polyisoprenes.[16] The NMR data (supported by DEPT) show signals which relate both to sp^2 and sp^3 carbon atoms involved in C-H and C-C bonds. Isoprene, however, is a C_5H_8 molecule which is exactly half of that of β-myrcene. DTMS and Py-GCMS indicated that the best candidate is a poly-monoterpene. The chemical shifts and intensities of the peaks in the ^{13}C-NMR spectrum show a remarkable similarity to that of *cis*-1,4-poly-β-myrcene (Table, Scheme 1) that has been synthesised and characterised by Newmark and Majumdar and others.[17]

The NMR spectra show some 20 additional peaks (Fig. 4), mostly corresponding to aliphatic carbons of which the abundance is too high to originate from low molecular weight compounds. They may be explained by the presence of additional (yet unknown) monomeric units or by products of intramolecular cyclisation produced in the polymerisation process.[18] Small signals at 109.5 and 152.0 ppm suggest that some 3,4-polymerisation product (Scheme 1) of β-myrcene is present. In addition, several (broadened) peaks as well as information from 2D and DETP NMR suggest that the β-myrcene units partly have a *trans*-configuration. For example, the broadened peaks at 30.5 and 29.2 may be explained by C_1 and C_4 in the *cis*/*trans* mode, respectively. The chemical shifts of the other carbon atoms are anticipated to be similar and to cause some peak broadening at the most. The ratio of *cis*- and *trans*-poly-β-myrcene is estimated as 3/1 based on the integrated signals at for C_1 at 31.5 and 30.5 ppm.

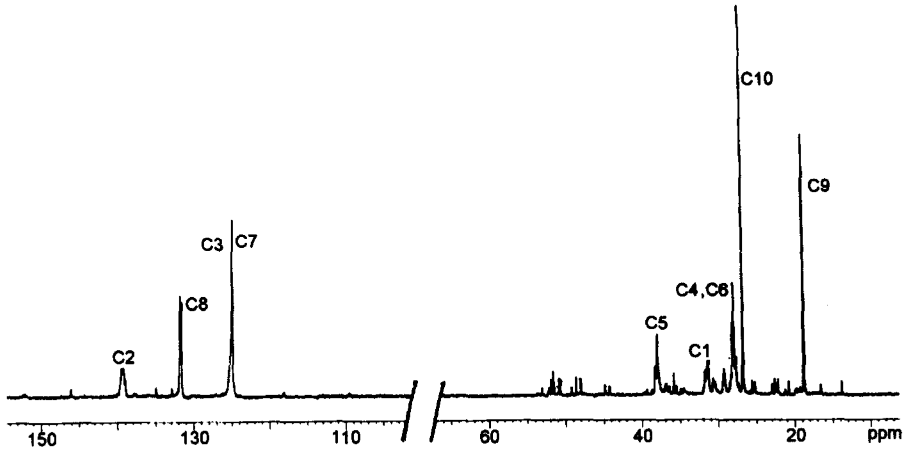
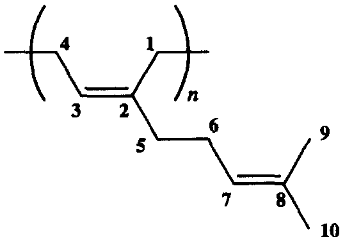


Figure 4. ^{13}C-NMR spectrum ($C_2D_2Cl_4$) of the polymer fraction of gum mastic.

Table. Chemical shifts and intensities of the relevant peaks in the ^{13}C-NMR spectra of mastic polymer fraction and synthetic *cis*-1,4-poly-β-myrcene.[17]

	Polymer of gum mastic		Synthetic Polymer	
Assignment	Chemical Shift	Intensity (integral)	Chemical Shift	Intensity (peak heights)
C_1	31.5	80	30.56	148
C_2	139.5	92	138.86	99
C_3	125.0	100	124.52	102
C_4	28.1	80	26.74	147
C_5	38.1	98	36.85	193
C_6	27.8	84	26.92	300
C_7	125.0	100	124.36	225
C_8	131.8	118	131.01	22
C_9	18.8	130	17.64	182
C_{10}	26.7	118	25.62	400

Scheme 1. *Cis*-1,4-poly-β-myrcene.

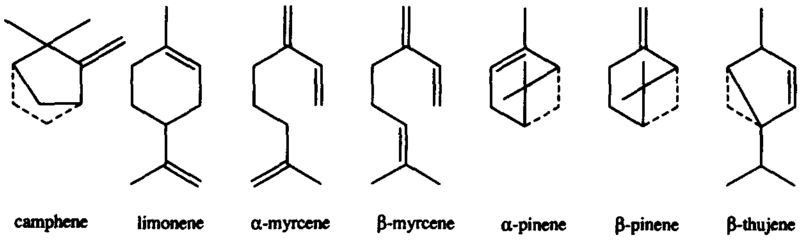


Little or no evidence for products of oxidation or oxidative cross-linking is found. Chemical shifts of 60 ppm or more are expected to correspond to sp^3 C-O functionalities which are not present in any manifest abundance. Therefore the oxygen-containing species analysed by Py-GCMS and FT-IR analysis (C=O bend vibration at 1700 cm^{-1}) may well be explained by the triterpenoid impurities and possibly some phtalate (Fig. 3).

The polymer proved to be relatively unstable after isolation when no precautions to avoid degradation were taken which was indicated by the rapid decrease of solubility of the polymer after isolation. This suggests that, due to the large number of unsaturations, oxidation and/or cross-linking takes place rapidly. In addition, the *cis*/*trans* isomerisation may have taken place. The instability of the poly-β-myrcene may hamper the positive identification of this polymer in, for example, aged varnish samples from paintings. The degraded polymer was not investigated at this stage; this will be done in future research.

In conclusion, the polymeric fraction of mastic from *Pistacia lentiscus* L. is 1,4-poly-β-myrcene which has the *cis*-conformation for about 75%. Analysis of the oil of turpentine content of mastic teardrops (which makes up for only 2%) showed that α-pinene is the most abundant compound.[19] In addition, also β-myrcene and low amounts of limonene, camphene and β-pinene were identified. Of these compounds, β-myrcene is the only compound with conjugated double bonds which are relatively prone to polymerisation (Scheme 2). We infer that the tree produces relatively large amounts of β-myrcene which is polymerised once the resin exudes from the tree. The reason why *P. terebinthus* L. produces a turpentine rather than a solid resin might then be explained by relatively low amounts of myrcene and relatively high

Scheme 2. Monoterpenes



amounts of non-polymerisable essential oil compounds. Monoterpenes such as β-myrcene are relatively common components of the volatile fraction of tree balsams[4] and it is also known to be secreted by butterflies.[20] Polymers of isoprenes (natural rubber),[16] polysesquiterpenoids (polycadinene) and polyditerpenoids (e.g. polycommunic acid)[1,13,21] have been known for a long time. This new discovery is important since it is the first reported naturally occurring polymer of a monoterpene.

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