



Terpenoid composition and chemotaxonomic aspects of Miocene amber from the Koroglu Mountains, Turkey



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ARTICLE INFO

Article history:

Received 29 August 2013

Accepted 15 October 2013

Available online 24 October 2013

Keywords:

Cretaceous amber

Turkey

Chemotaxonomy

Terpenoids

Pinaceae

ABSTRACT

A recently discovered fossil resin from Koroglu Mountain in Turkey has been analyzed by gas chromatography–mass spectrometry and pyrolysis gas chromatography–mass spectrometry to determine its structural class and botanical origin. The sesqui- and diterpenoids contained in the amber extract were used as chemosystematic markers when compared with terpenoids in extant conifers. The pyrolysis products were dominated by labdanoid derived bicyclic products together with succinic acid indicating Class Ia type amber. The biomarker compositions of the resin comprise mainly sesqui- and diterpenoids, and lack triterpenoids. This distribution suggests a gymnosperm, and more specifically a conifer source. The exclusive presence of abietane- and labdane-type diterpenoids together with the absence of phenolic diterpenoids strongly suggest that the resin was derived from Pinaceae. However, the presence of methyl-16,17-dinor callitrisate in the pyrolysate also suggests that Cupressaceae cannot be excluded as a possible source for the amber.

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1. Introduction

Amber is fossilized tree resin that occurs naturally as lumps or layers in sediments and coals. Plant resins consist of a complex mixture of mono-, sesqui-, di- and triterpenoids and/or phenolic compounds [1–4]. Mono- and sesquiterpenoids are volatile components of plant resins and are gradually lost when exposed to the atmosphere. During fossilization, the original bioterpenoids undergo some minor diagenetic transformation to form geoterpenoids which are found in amber [5]. Despite various chemical alterations processes that occur during diagenesis, the geoterpenoids still retain the basic skeletal structures of their biological precursors and can be used as chemosystematic markers [6–9]. Therefore, knowledge about the chemical composition of ambers

can provide evidence about their botanical origin, ancient terrigenous ecosystem and climatic change [10–14]. Diterpenoids are the major products of conifer (gymnosperm) – derived resins whereas triterpenoids (e.g. oleanane, ursane and lupane) are products of angiosperm resins [9,15,16]. The determination of the geographic origin of amber collected from archeological objects is also of great importance in drawing the map of cultural and trade networks among primitive human settlements [17–22].

Gas chromatography–mass spectrometry (GC–MS) and pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS) are useful methods for elucidating the molecular composition of ambers [11,23–30]. While the GC–MS allows only (semi-) volatile organic soluble components, which rarely account for more than 20% of the whole resin, to be identified, Py-GC–MS has the advantage of breaking polymeric constituents, insoluble and non-volatile macromolecules present in amber into smaller and highly volatile molecules that can be analyzed by GC–MS.

Amber has been recently discovered in northern Turkey, near Bolu in the Koroglu Mountains. This is a zone of young tectonic folding, with an area of young volcanic activity to the east [31]. The rock in which the resin was found has been identified as fine-grained but poorly sorted wacke sandstone (greywacke). The resin is found in rock in the form of pebbles, but also in dripstone and classic form [31]. Most of the volcanism in the region appears to be Miocene or earlier, therefore it is possible that the amber is Miocene

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in age [31,32]. The resin has been reported to resemble Cretaceous amber from Burma, Romanite from Romania's Neogene Carpathian flysch and Palaeogene Romanite from Sakhalin based on its infrared spectroscopy features [31]. In this study, the terpenoid composition of the fossil resin from Koroglu Mountain, Turkey was analyzed by GC–MS and Py–GC–MS in order to determine its botanical source. To the best of our knowledge, this study reports the first information on the terpenoid composition and botanical origin of amber from Koroglu Mountain, Turkey.

2. Samples and methods

2.1. Sample

The amber was discovered in 2009 by Tafun Baser in the Western Pontic Mountains 'west Black Sea' at an altitude of 1600 m and depth of 50 cm. The exact location was not recorded but the discoverer reported that the resin's accumulation is located in northern Turkey, near Bolu in the Köroglu, Mountains [31]. The sample was donated to Hunterian Museum (accession number GLAHM 131710) of the University of Glasgow, United Kingdom by Nigel Berrington in 2011. A sample for the present study was taken from a freshly exposed scratch surface to avoid the effect of any possible oxidative weathering.

2.2. Extraction and derivatization

The powdered sample (ca. 200 mg) was sonicated (3×15 min) with dichloromethane:methanol (1:1; v/v). The combined extracts were filtered, evaporated with a rotary evaporator to approximately 1 ml, transferred to a vial and the residual solvent was removed under N_2 . The total extract yield was 38.6 mg which represents 19.3% of the original amber. An aliquot of the total extract was converted to trimethylsilyl derivatives by reaction with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) for 3 h at 70 °C.

2.3. GC–MS

GC–MS analysis of the derivatized extracts was performed on an Agilent 6890 GC coupled to an Agilent 5973N quadrupole mass selective detector. Separation was achieved on a fused silica capillary column with Rtx-5MS (30 m \times 0.25 mm i.d., d_f : 0.25 μ m film). The GC oven was programmed as follows: initial temperature 60 °C (held 2 min), 6 °C min^{-1} to 300 °C (held 10 min). Helium was used as carrier gas at constant flow rate of 1.0 ml/min. Samples were injected in splitless mode with the injector temperature at 290 °C. The mass spectrometer was operated in the full scan mode from 50 to 650 amu and with electron impact ionization at 70 eV. Data were acquired and processed using Chemstation software. Individual compounds were identified by comparison of mass spectra with literature and NIST MS Library data [7,8,11,12,26,33–35].

2.4. Py–GC–MS

Pulverized amber (~ 200 μ g) was pyrolyzed at 480 °C for 20 s using a Thermal desorption unit with pyrolysis module (TDU P) (Gerstel GmbH & Co. KG) coupled directly to an Agilent 7890 GC system and an Agilent 5975 B Mass Selective Detector (MSD). The sample was pyrolyzed in the presence of tetramethylammonium hydroxide (TMAH) to ensure methylation of liberated polar functional group products. The GC was operated in split mode and was equipped with a DB5 fused silica column (30 m \times 0.25 mm i.d., 0.25 μ m film thickness). The GC oven operation conditions were: initial temperature held at 60 °C for 2 min, increased from 60 to 300 °C at a rate of 6 °C min^{-1} (held 10 min). Helium was used as

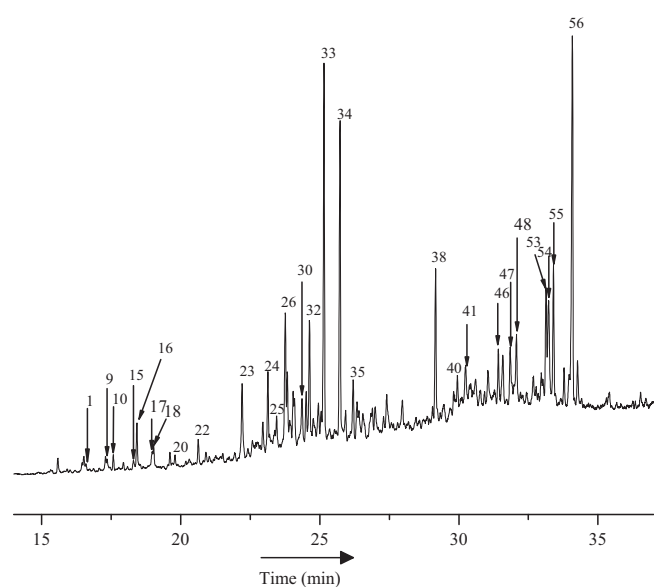


Fig. 1. GC–MS total ion chromatograms (TICs) of derivatized extract of Cretaceous amber from Koroglu Mountains, Turkey (peaks assignments correspond to product list in Table 1).

carrier gas at constant flow rate of 1.0 ml/min. The mass spectrometer was operated in the electron impact mode at ionization energy of 70 eV and a source temperature of 260 °C. Full scan mass spectra were recorded over a mass range from 50 to 650 amu and data were acquired and processed using Chemstation software. Individual compounds were identified based on comparison of MS data with literature and NIST MS Library data [7,8,11,12,26,33–35].

3. Results and discussion

3.1. Molecular composition of amber extract

The total ion chromatogram (TIC) from the GC–MS analyses of the derivatized extract of the amber is presented in Fig. 1. The compounds identified in the extract together with their mass spectrometric data are listed in Table 1. The extract contains alkyl benzenes (2, 9, 10 and 17) and alkyl naphthalene (5 and 22). 4 β -Eudesmane (15) and dihydrocadinene (20) were the only sesquiterpenoids detected in the resin extract. Some diagenetic products of sesquiterpenoids such as ionene (16) and methylionene (19) were also detected. The extract is dominated by abietane and labdane-type diterpenoids. The abietane class diterpenoids comprised of 16,17,19-trisnorabietane (24), bisnorabietane isomer (31), 16,17,19-trisnorabieta-8,11,13-triene (33), bisnorabietane (34), 16,17-bisnordehydroabietane (38) and 16,17-bisnordehydroabiatic acid (46). The labdanes included E and Z-19-noragathic acids (40 and 41) and 13-dihydro-19-noragathic acid (47). Podocarp-13-en-12-one (27) and 8,13-dimethyl-16-norpodocarpa-6-ene (35) belonging to podocarpane class diterpenoids were also detected in the sample. The identities of some of the peaks (48, 53 and 54) cannot, at present be assigned.

3.2. Molecular composition of amber pyrolysate

Most of the compounds identified in the amber extract were also detected in the pyrolysate (Fig. 2) indicating that the compounds are present as occluded materials that are not bound into the macromolecular network of the amber. However, an additional sesquiterpenoid, 5,6,7,8-tetrahydrocadalene (21)

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