3 The Neolithic in the Middle Morava Valley

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The Neolithic in the Middle Morava Valley

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The Neolithic in the Middle Morava Valley:

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In memoriam Radovan Petrović

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Chemical analysis of tarry materials found on pottery from Neolithic settlements in Serbia

Abstract:

In the current study, samples from three Neolithic settlements located in different geographical areas in Serbia; Starčevo–Grad, Drenovac and Pavlovac–Gumnište, were selected in order to determine whether the materials used to seal and repair ceramic pots from this specific region were of the same botanical source as in other regions of Neolithic Greece and the Balkans; and whether they were produced using the same technology as the other similar resinous materials. The ancient organic residues were analysed using the gas chromatography-mass spectrometry (GC-MS) technique, while the determination of their composition was made by identifying diagnostic components (biomarkers). The study revealed that the resinous material was tar produced by the pyrolysis of birch bark
Keywords: Middle Neolithic, Late Neolithic, pottery, organic residue analysis, birch bark tar, ancient repairs

INTRODUCTION

Higher plant resins and related substances have been widely used since prehistory for a variety of purposes such as glues, coating, decorating, protecting and sealing agents in everyday life, either in their natural form or submitted to treatments before use, e.g. preparation of pitch and tar by hard-heating of resins or resinous wood.[1] The chemical composition of resins and tars is commonly used as evidence of the usage, the manufacturing process and trade in Antiquity. Furthermore, the identification of biomolecular components formed under specific treatments is valuable for the study of ancient technologies.[2]

The use of fresh and fossilised plant exudates/tars in prehistory has been documented throughout Europe, with more references to its northern part. Greece and the prehistoric Balkans are still an unexplored area to a great extent, but with great potential, as was revealed in our recent studies. Our preliminary results from GC–MS organic residue analysis from potsherds preserved at Neolithic sites in northern Greece, confirmed the use of birch bark tar in this part of the Balkans, with some hints on the sporadic use of pine resin and pitch.[3] Further systematic study of the Neolithic tarry materials showed considerable variability in the composition of birch bark tar, possibly related to the production technique.[4]

1 Aveling, Heron 1998; Urem-Kotsou et al. 2002; Regert 2004.
2 Pollard, Heron 1996; Colombini, Modugno 2009.
3 Urem-Kotsou et al. 2002, 2004; Mitkidou et al. 2008.
4 Urem-Kotsou et al. 2018.

In the current study, samples from three Neolithic settlements in Serbia were selected in order to identify the resinous material used to seal and repair ceramic pots from this specific region and to compare the botanical source and the chemical composition with other resinous materials used in the same periods in other regions of Neolithic Greece and the Balkans. The ancient organic residues were analysed using the gas chromatography-mass spectrometry (GC-MS) technique, while the determination of their composition was made by identifying diagnostic components (biomarkers).

MATERIALS AND METHODS

Archaeological samples

The archaeological samples selected for the organic residue analysis in this work include tarry material found on pottery fragments from three Neolithic sites in Serbia: Drenovac, Pavlovac (Gumnište) and Starčevo. In total, 34 samples were analysed: 24 samples from Drenovac, 6 samples from Pavlovac (Gumnište) and 4 samples from Starčevo.

The site of Slatina–Turska česma, Drenovac, is located in the Middle Morava valley of Central Serbia. It is a multi-stratified site with deep cultural deposits up to 6.50 m thick, spanning the periods from the Early Neolithic – Starčevo culture (6100–5900 BC) to the Late Neolithic – Vinča culture (5300–4700/4500 BC). A geophysical survey revealed a large settlement area of around 40 ha that was very densely populated.[5] The samples analysed in this paper come from several excavation campaigns: 1969, 2004 and 2005. In 1969, excavations were carried out by Sava Vetnić from the Regional Museum in Jagodina. Since 2004, excavations at Drenovac have been conducted by the Institute of Archaeology (Belgrade), as part of the project *Permanent archaeological workshop – Middle Morava Valley in Neolithisation of South–East Europe*, and they are still ongoing.[6]

The site of Pavlovac–Gumnište is situated in the central part of the Vranjsko–Bujanovački basin in South Serbia, on a terrace on the left bank of the Južna Morava River, 7 km south-west of the modern city of Vranje. The site was occupied both in the Middle (Starčevo culture 5700–5400 BC[7] and the Late Neolithic (Vinča culture 5300–4700/4500BC). Samples of pottery analysed for the presence of resinous material come from the rescue excavations carried out in 2011 within the framework of the project aimed at protecting the archaeological heritage along the new route of the E75 highway.[8] Based on the characteristics of the motifs of painted decoration and the shapes of the vessels, the samples are dated to the later phase of the Starčevo culture, that is – Middle Neolithic of Central Balkans IIIa, according to the chronology proposed by N. N. Tasić [9].

The site of Grad – Starčevo is located in the vicinity of the modern city of Pančevo, in the Banat region of the Danube basin. According to the data provided by M. Živković, the Neolithic settlement spread across 11.3 ha.[10] Radiocarbon dating indicates that the settlement was occupied in three different phases between *c.* 5900 and 5500 BC, with some areas being used successively.[11] The painted pottery analysed in this work comes from the 1932 excavation season[12].

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5 Perić et al. 2016a.
6 Perić 2009, 2017.
7 Тасић 2009, 131–132.
8 Perić et al. 2016b.
9 Тасић 2009.
10 Živković et al. 2011, 7.
11 Whittle et al. 2002, 81.
12 Only sample STR 350 comes from the excavation season of 1932, while for others the year of excavation is unknown; Fewkes et al. 1933.

Preparation of archaeological samples

Adhering organic residues and a portion of ceramic potsherd (100–800 mg) were removed with a sterile scalpel and crushed into a powder. After the addition of n-tetratriacontane (internal standard, 30 μL of a 1 mg mL_{-1} solution in hexane HPLC grade Sigma), the organic powder residue was extracted with 10 mL of chloroform/ methanol (HPLC grade Sigma) 2:1 (*v/v*) by ultrasonication for 30 min. Following sonication, the test tube was placed in a centrifuge (20 min, 2000 rpm) to separate the solvent mixture from the inorganic clay particles. After centrifugation the extract was filtered through solvent-washed silica gel (SPE bond elute C18) and an aliquot (1/2) evaporated under a stream of nitrogen. The dry total lipid extract was derivatized by treatment (50 μL, at 75°C, for 30 min) with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing 1% *v/v* trimethylchlorosilane (Pierce Chemical Co.). After cooling to ambient temperature and the evaporation of the excess of BSTFA under a gentle stream of nitrogen, the resulting trimethylsilyl (TMS) derivatives were diluted in hexane (100–200 μL). Combined gas chromatography-mass spectrometry (GC-MS) was then carried out.

Gas chromatography–mass spectrometry analyses

Analyses were carried out on a 6890 Agilent Gas Chromatograph (GC) with splitless injection, coupled to a 5975B Mass Spectrometer system (MS). The GC was fitted with a 30 m long, 0.25 mm id, 0.1μm film thickness DB-5MS column, preceded by a 1 m deactivated precolumn. The oven temperature was increased from 50°C (held isothermally for 2 min) to 320°C at 10°C min^{-1} (held isothermally for 15 min). Helium was used as the carrier gas at a constant flow rate of 1.2 mL min^{-1}. The MS transfer line temperature was 280°C; the MS ion source temperature was kept at 230°C and the MS quadrupole temperature was at 150°C. Mass spectra peak assignments were based on a comparison with the internal mass spectrum databank (from commercial standards and from fresh and artificially aged resins) and the NIST databank (NIST MS Search 2.0).

RESULTS AND DISCUSSION

The analysis of the archaeological samples and the similarity to the reference birch bark extract and tar chromatograms revealed that birch bark tar, a triterpenic material prepared by the pyrolysis of birch bark, was the material primarily used as an adhesive for repairing and sealing the sampled ceramic pots. Particularly, compounds with a base peak at *m/z* 189 characteristic of triterpenoid molecules with a lupane skeleton, already well known as extractive components of birch bark, were found in a relatively large number of samples (10 out of 34), given that visible residues are not common in pottery assemblages and are prone to post-burial and post-excavation loss during the cleaning of the sherds. These include betulin, lupeol, lupa-2,20(29)-dien-28-ol, lupenone, triterpenoid hydrocarbons of the formula $C_{30}H_{48}$ and $C_{30}H_{50}$, allobetulene and, in a few samples, betulone. Table 1 shows the triterpenoid compounds that were found in the archaeological samples, indicating that the resinous materials identified were produced from the same botanical source. The chromatograms from Serbian archaeological samples show a similar pattern to Greek samples from the same period[13], as the example of partial total ion chromatograms (TICs) of one sample from Drenovac (DR1) and one from Paliambela Kolindrou, northern Greece (PL8) in Figure 1 shows.

When birch bark is heated, changes in resin composition occur, leading to the formation of tar. The presence of a high amount of the known degradation products of lupeol and betulin in most of the samples, namely lupa-2,20(29)-diene and lupa-2,20(29)-dien-28-ol, suggests that the archaeological tars were obtained by the pyrolysis of birch bark in all cases except sample DR2.

13 Urem-Kotsou et al. 2018.

	LUPADIENE, $C_{30}H_{48}$	$C_{30}H_{50}$	LUPADIENOL -TMS	ALLO -BETULENE	LUPENONE	LUPEOL-TMS	BETULONE -TMS	BETULINE -bis-TMS	BETULINIC ACID bis-TMS	ALLO-BETULINOL	M.Bio/D.M.
SAMPLE											
DR1	3,08	1,73	18,92	28,94	6,7	4,72	6,54	28,15	3,55	1,47	0,7
DR2						8,29		91,71			M.Bio
DR11	7,46	1,03	13,7	4,19	2,78	15,73	tr	32,8	tr	3,09	1,9
DR17	2,5	1,74	14,52	5,43	2,84	12,72	4,02	33,34	1,59	1,68	2
DR20	14,47	7,3	15,06	8,13	4,95	12,14	2,25	16,42	tr	1,05	0,8
DR23	24,5	13,42	2,11	13,47	2,98	14,73	tr	7,4	tr	tr	0,6
PGM188	14,33	12,93	19,85	9,45		tr		2,98			D.M.
PGM215	5,15	2,31	43,61	15,16							D.M.
STR350	8,23	1,87	15,99	2,3	5,32	15,38	6,82	35,84		tr	1,9
STR587	5,21	3,37	15,54	4,23	4,9	8,74	7,63	33,44		tr	1,7

Table 1 – Relative percentages of compounds identified by GC/MS in archaeological samples and their diagnostic fragments

Although lupa-2,20(29)-diene and lupa2,20(29)-dien-28-ol are also known to be formed by natural decay within the sedimentary matrix[14], the ratio between the major biomarkers (lupeol and betulin) and the degradation markers (lupadiene, lupadineol, allobetulene) (Tab. 1) may be used as an indicator of the production process. The composition of the DR2 sample resembles the composition of the extract of birch bark, since heating derivatives of birch bark tar were not identified in this sample (Fig. 2).

The results of the analyses showed that birch bark tar was mainly used in a pure form. The possible mixing of tar from birch bark with animal fat was found in three (3) samples from Drenovac. The mixing of tar with animal fat is considered to be a practice identified in the Neolithic settlements in northern Greece, but also in other regions.[15]

Drenovac

In total, 24 samples with prominent black residues were studied to determine their natural origin. The specimens are dated to the Late Neolithic period. Organic residues were found in eight samples out of 24 (Tab. 1; T. I). In six samples (DR1, DR2, DR11, DR17, DR20, DR23) the black residue was used for gluing and sealing the vessels. In the DR23 sample there were visible residues (probably for sealing) from both the inner (DR23es) and the outer side (DR23ex) of the vessel; so, both sides were examined comprehensively.

Samples characterised by the presence of tar from birch bark

Six (6) samples DR1, DR2, DR11, DR17, DR20 and DR23 (DRes, DRex) revealed the presence of triterpenic biomarkers of the lupane family, which characterise tar from birch bark. The basic components of birch bark, betulin and lupeol, were identified in the DR1, DR11, DR17, DR20,

14 Aveling and Heron 1998; Rageot et al. 2019.
15 Urem-Kotsou et al. 2018 and references therein.

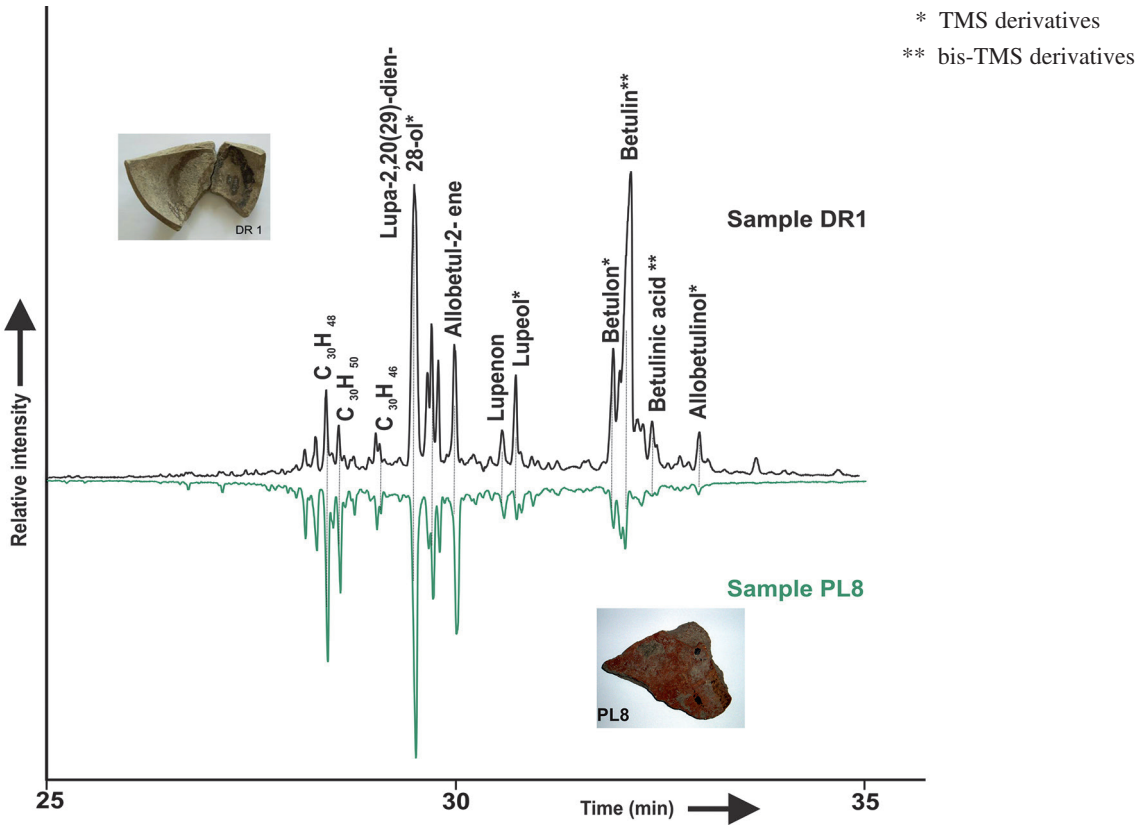

Figure 1. Comparison of gas chromatograms in the diagnostic ion (m/z = 189) of the samples DR1 (Drenovac) and PL8 (Paliambela-Kolindrou)

$DR23_{es}$ $DR23_{ex}$ samples, as well as their degradation products lupa-2,20(29)-dien-29-ol, lupa-2,20(20)-diene ($C_{30}H_{48}$), which prove that the material used to seal and repair the vessels was tar resulting from the pyrolysis of birch bark. In the DR2 sample only the basic components of birch bark, betulin and lupeol, were found (Fig. 2).

Several experimental studies have shown that the chemical composition of the tar made from birch bark depends on the production temperature.[16] At around 400°C, the amount of betulin decreases sharply as there is a simultaneous increase in degradation products. With a higher temperature and warm-up period, betulin and lupeol are the first components that disappear completely.[17] Sauter (1988) firstly reported findings of birch pitch with little or no betulin; while Regert and Rolando (1996), and Regert (2004) described the reactions that took place at high temperatures and led to the formation of so-called degradation markers (lupenone, allobetulene, lupadiene, etc.).

On the basis of the presence / absence and the proportion of the major birch bark tar biomarkers and their degradation compounds, it was found that the archaeological samples show compositional differences from one sample to another, indicating that the degree of conversion of the key biomarkers into degradation products is different. For each sample, the M.Bio / D.M (Main Biomarkers / Degradation Markers) ratio was calculated among the key biomarkers (betulin, lupeol, betulone, lupeol, betulinic acid) and the degradation products (hydrocarbons $C_{30}H_{46}$,

16 Rageot et al. 2019.
17 Dudd and Evershed 1999; Regert 2004; Perthuison et al. 2020.

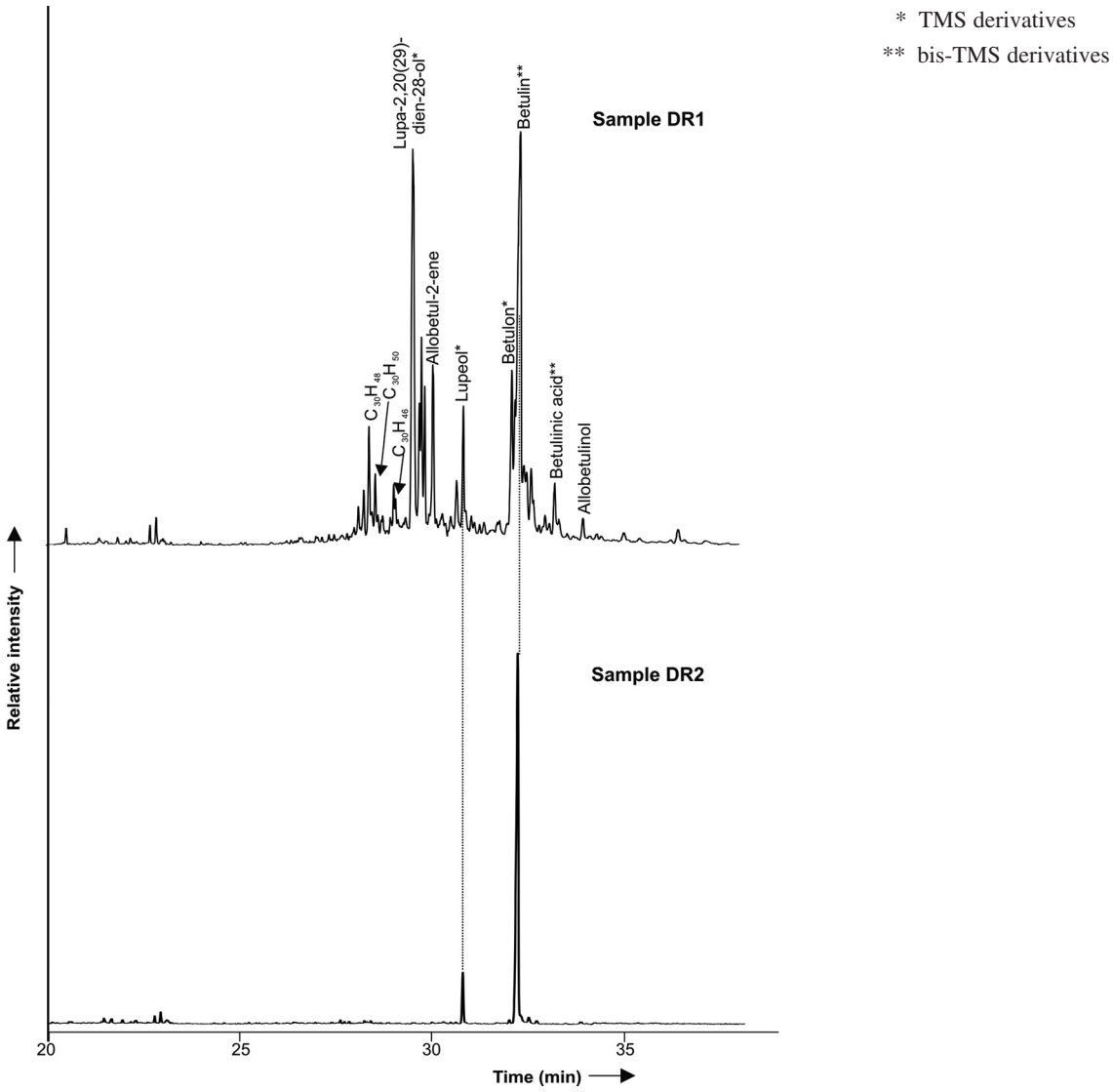

Figure 2. Comparison of gas chromatographs in the diagnostic ion (m/z = 189) of the samples DR1 and DR2

$C_{30}H_{48}$, $C_{30}H_{50}$, Lupa-2,20(29)-dien-28-ol, allbetul-2-ene, allobetulinol). Following Regert (2004), the samples were classified in relation to the ratio M.Bio / D.M. into three categories, which determined the way the tar was prepared and the pyrolysis temperature:

a) Samples in which the basic components are found to be at a higher ratio (M.Bio / D.M> 1.2). This category includes the DR2, DR11 and DR17 samples. The high proportion of basic components in relation to the degradation products suggests that in these samples the tar was prepared under mild heating conditions of approximately 350°C.[18] Particularly in the DR2 sample, only the basic components of tar, betulin and lupeol were identified. The same chromatographic profile was also observed in a sample from the Makriyalos settlement[19], in which only the basic components of tar were also detected.

18 Charters et al. 1993.
19 Mitkidou et al. 2008.

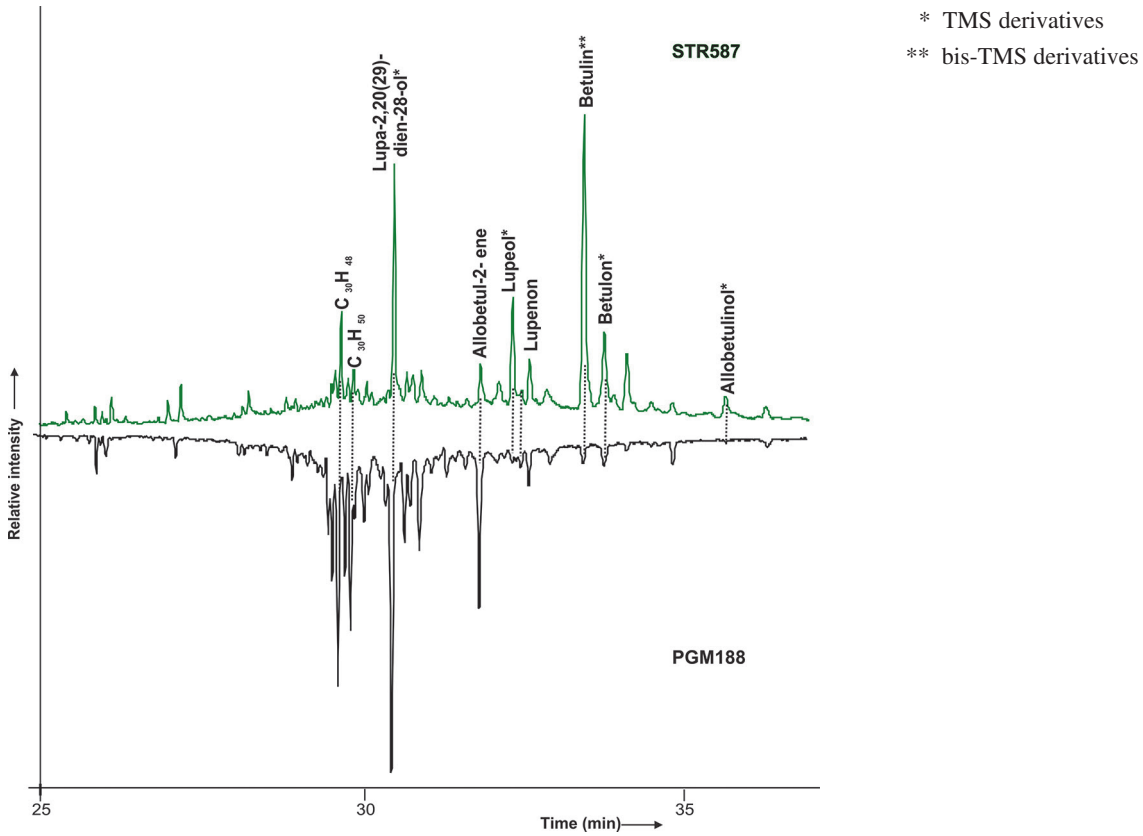

Figure 3. Comparison of gas chromatographs in the diagnostic ion (m/z = 189) of the samples STR587 and PGM188

b) Samples in which the degradation products (M.Bio/D.M<0.8) are in a much greater proportion than the basic components. This category includes the DR20 and DR23 samples. In these samples it seems that tar was prepared at a very high temperature (over 400°C) and with prolonged heating, as it is known that under these conditions the quantity of degradation products is significantly increased.[20]

c) Samples in which there is no significant differentiation between the ratio of the basic components and the degradation products (0.8<M.Bio/D.M<1.2). The DR1 sample belongs to this category. The tar in this particular sample appears to have been prepared at temperatures between 350–400°C.

Taking into consideration the above results, it is apparent that in Neolithic Drenovac there was no specific recipe for the preparation of tar from birch bark. The different relative proportions (Fig. 4) in the basic components and degradation products showed that different pyrolysis conditions were applied, sometimes more intense and sometimes less. The chromatographic data of the samples from several Neolithic settlements in northern Greece and the settlement at Drenovac showed considerable similarities both in the composition and the relative proportions of the individual components.[21] A typical example is given in Figure 1, where the chromatograms are compared to the *m/z* 189 diagnostic ion of the DR20 (Drenovac) and PL8 (Paliambela-Kolindrou) samples.

20 Charters et al. 1993; Koller et al. 2001.
21 Urem-Kotsou et al. 2018.

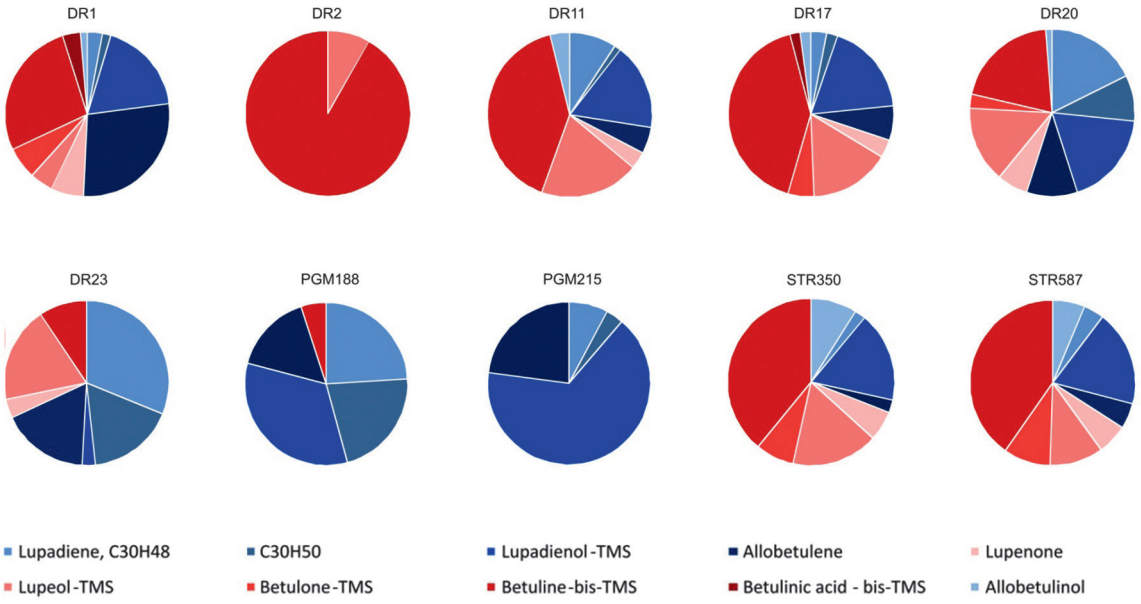

Figure 4. The relative percentages (%) of the triterpenoids identified in the samples from the three Neolithic settlements in Serbia. The areas of blue represent degradation markers, while areas of pink and red are the basic components of birch bark tar

Samples with the presence of a fatty substance

In addition to the characteristic compounds of tar from birch bark, a small amount of cholesterol and saturated fatty acids with a small carbon chain (palmitic acid ($C_{16:0}$) and stearic acid ($C_{18:0}$) were detected in three samples; DR1, DR2 and DR11. The high proportion of stearic acid in relation to palmitic acid and the presence of small amounts of cholesterol suggest the mixing of birch bark tar with animal fat. The presence of fatty acids in birch bark tar has also been detected in archaeological samples in other parts of Europe, as in the case of a Roman vessel, where tar was used as an adhesive[22], and in the case of a vessel (cup) from Hougue Bieregion (Jersey), in which birch bark tar was used as an aromatic material[23]. The addition of animal fat may be related with the production technology of the tar.

In the DR1 sample, besides the animal fat and the birch bark tar components, GC-MS analysis revealed the presence of two late-eluting high-molecular-weight triterpene compounds. With these compounds, although no molecular ion was detected, their retention time, their mass spectrum, and the presence of fatty acids in the sample are serious indications that they are probably esters of lupa-2,20(29)-dien-28-ol formed from the heating of fat and birch bark[24]. Similar compounds have been reported by Regert (2007) in two samples from the Neolithic region of Bercy (France), and were also identified in a jar of the Roman period from the Catterick area (N. Yorkshire, UK), where a series of fatty acid triterpenic esters were reported[25]. The existence of these compounds along with the presence of cholesterol in the DR1 sample strengthens the assumption that animal fat was likely mixed with birch bark tar in this sample.

22 Charters et al. 1993.
23 Lucquin et al. 2007.
24 For more details see Urem-Kotsou et al. 2018.
25 Dudd, Evershed 1999.

Sample	Site	Context	Excavation year	Relative chronology	Vessel type	Part of the vessel
PGM 188	Pavlovac Gumnište	Trench II, B11, layer 10	2011	Middle Neolithic	Painted pottery, bowl	Rim
PGM 215	Pavlovac Gumnište	Trench II, C12, layer 5	2011	Middle Neolithic	Painted pottery, unknown	Lower body
STR 350	Starčevo	Settlement, Pit 5A, BL north	1932	Middle Neolithic	Painted pottery/ unknown	Body
STR 587	Starčevo	Trench A	Unknown	Middle Neolithic	Painted pottery/ unknown	Body
DR 1	Drenovac	Trench V, excavation layer 9, northern half	1969	Late Neolithic	–	Base and lower body
DR 2	Drenovac, Turska česma, Slatina	Trench XV, removal of floor of house 1	2004	Late Neolithic	Tableware decorated with rippled decoration	Rim
DR 11	Drenovac, Turska česma, Slatina	Trench XV, square 3, excavation layer 43–47, beside western AD profile	2005	Late Neolithic	–	Body
DR 17	Without label	Unknown	Unknown	Late Neolithic	Pedestall vessel with red burnished outer surface	Foot
DR 20	Drenovac, Turska česma, Slatina	Trench XV, square 3, excavation layer 45–47, ramp beside eastern BC profile	2005	Late Neolithic	Black burnished vessel	Body
DR 23	Drenovac, Turska česma, Slatina	Trench XV, square 1, excavation layer 18	2005	Late Neolithic	Black burnished vessel	Body

Table 2 – Additional information about the archaeological samples with identified ancient tarry remains

Identification of pine pitch

In addition, in the DR1 sample, diterpenoids characteristic of pine resin were also detected. Particularly, isopimaric acid and dehydroabietic acid (DHA), which is the most abundant molecule in aged Pinus samples, as well as 7-oxodehydroabietic acid and dehydro-dehydroabietic acid, characteristic oxidation products of DHA, were identified. A parallel use of birch bark tar and pine resin in archaeological pottery is not unknown.[26] Regert et al. (2000) reported the presence of pine pitch along with birch bark tar as a result of the repeated use of two different adhesive materials and not as an intentional use as a mixture. Pine resin and pitch have also been identified in several samples at Neolithic settlements in northern Greece.[27]

Pavlovac–Gumnište

From the Neolithic settlement of Pavlovac –Gumnište, four samples of pots of unknown use with traces of material used as adhesive were analysed. GC-MS analysis of the organic extract of the samples revealed the presence of organic residues in two of them (PGM188 and PGM215; Tab. 1). In both of these samples, the high amounts of the hydrocarbons $C_{30}H_{46}$, $C_{30}H_{48}$, $C_{30}H_{50}$, lupa-2,20(29)-dien-28-ol and allobetulene, suggest that the archaeological tars were obtained by the pyrolysis of birch bark at particularly high temperatures. In PGM188 only a small quantity of the main biomarkers, namely lupeol and betulin, of tar from birch bark were detected, while in the PGM215 sample both main biomarkers were absent (Fig. 3).

26 Pollard and Heron, 1996, 256–257; Regert et al. 2000.
27 Urem-Kotsou et al. 2018.

Starčevo

From the Neolithic settlement of Starčevo, six samples from vessels of unknown use with traces of material used as adhesive for repairing broken pots were analysed. The results of chemical analysis confirmed the use of tar made from the pyrolysis of birch bark in two cases. Specifically, in the two samples STR350 and STR587 (T. I), large amounts of the main biomarkers, lupeol and betulin, along with relatively smaller amounts of their degradation products, the hydrocarbons $C_{30}H_{46}$, $C_{30}H_{48}$, $C_{30}H_{50}$, lupa-2,20(29)-dien-28-ol and allobetulene were detected (Tab. 1), suggesting a relatively low temperature applied in the production of tar (Fig. 3).

CONCLUSIONS

The GC-MS study of ancient tarry remains from the three Neolithic settlements located in different geographical areas in Serbia revealed that the nature of the resinous material used during the Neolithic in order to seal and repair the pottery was tar produced by the pyrolysis of birch bark. The results of the analyses from Drenovac show variations in the composition of birch bark tar that strongly resemble samples from Neolithic settlements in northern Greece (especially from the Late Neolithic period), which are mainly attributable to a variation in the temperatures applied during the pyrolysis of birch bark. As the samples from Drenovac suggest, the conditions for the preparation of tar varied considerably as there are quantitative differences between the initial components of birch bark and their degradation products. In addition, the presence of triterpenic esters with fatty acid indicates that tar may have been mixed with animal fat. According to the results of the study presented here, tar was used at Drenovac in a pure form and occasionally mixed with animal fat and, in one case, with pine pitch. In the Pavlovac–Gumnište settlement, the number of samples was very small, but the results showed that tar production took place at very high temperatures. Conversely, in the settlement at Starčevo, the results of the analysis of two samples, in which organic residues were detected, revealed that the pyrolysis of birch bark for the production of tar occurred at lower temperatures.

The likelihood of a common point of geographical origin for the birch bark tar used in the samples analysed is, for the time being, uncertain since a more detailed study of the light stable isotopic (δD, δ13C and δ18O) values await the results of ongoing research, which is expected to provide evidence as to whether the Neolithic birch bark tars were made locally or were traded. According to the study reported by Stern, the δ13C increases in fractionation with an increase in latitude, as is observed in samples from Greece, which are less depleted than those from northern Europe.[28] This observation opens up the potential of tracing the geographical origin of birch bark tar. Regardless of the uncertainty of the geographical provenance, the results of our study showed, however, that birch bark tar was as widely used in the Balkans hinterland as it was across Europe during the Neolithic period, including the regions of the Northern Aegean.

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28 Stern et al. 2006.

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Резиме

Хемијске анализе остатака катрана са керамике из неолитских насеља у Србији

У овој студији анализирани су узорци из три неолитска насеља, смештена у различитим географским областима у Србији: Старчево–Град, Дреновац и Павловац–Гумниште, да би се утврдило да ли су материјали коришћени за премазивање и поправку керамичких посуда из овог специфичног региона истог порекла као и у осталим регионима неолитске Грчке и Балкана и да ли су произведени истом технологијом као и други слични смоласти материјали. Органски остаци анализирани су техником гасне хроматографије-масене спектрометрије (GC-MS), док је одређивање њиховог састава извршено идентификовањем дијагностичких компоненти (биомаркера). Студија је открила да је смоласти материјал био катран произведен пиролизом коре брезе. Резултати анализа узорака из Дреновца показују варијације у саставу катрана од брезе, која веома подсећа на узорке из неолитских насеља у северној Грчкој (посебно из касног неолита), а које се углавном могу приписати разликама у температурама примењеним током пиролизе коре брезе. Као што указују узорци из Дреновца, услови за припрему катрана знатно су варирали јер постоје квантитативне разлике између почетних компоненти коре брезе и њихових продуката разградње. Катран се користио у чистом облику и повремено се мешао са животињском масноћом и у једном случају са боровом смолом. У насељу Павловац–Гумниште број узорака је био врло мали, али резултати су показали да се производња катрана одвијала на веома високим температурама. Супротно томе, у насељу Старчево резултати анализе два узорка, у којима су откривени органски остаци, открили су да се пиролиза коре брезе за производњу катрана одвијала на нижим температурама.

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