Studies in organic archaeometry III [1]. Prehistoric adhesives: alternatives to birch bark pitch[2] could be ruled out

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Abstract
The prehistoric adhesive used in central and northern Europe was most frequently prepared from the bark of the birch by means of a thermic process, usually assumed to have been pyrolysis to yield (via the intermediate step of a tar) a pitch. In order to rule out that the ancient products might have been made either by a simple extraction or — even more simply — by using a natural sap, such starting materials were studied. Although after drying up and heating both showed reasonably good adhesive properties, the ^{13}C-nmr spectra were remarkably different from those obtained from prehistoric agglutinants, e.g., giving no indication for the presence of betulin. Thus these two conceivable alternatives for the ancient preparation of the material in question can now be ruled out: the prehistoric adhesives can really be considered as pitch, prepared from the bark of the birch.

Keywords: Archaeometry, birch bark pitch, ^{13}C nmr spectroscopy, betulin

Introduction

In excavation sites of central and northern Europe dark organic materials are frequently found, which were used in prehistoric times for many purposes, in particular as adhesives and as coatings on pottery. Disregarding here the sometimes inexact terminology (which frequently does not distinguish between pitch and resin) such materials were mostly considered since the 19th century as *birch bark pitch* — first as a pure hypothesis (e.g., because of its characteristic smell upon heating),[3] later — beginning with Sandermann[4] — based on various methods of chemical analysis.[5]

Practically all the analytical studies were based

- either on comparisons between the archaeological material and laboratory-made ”model pitches” prepared by pyrolysis of birch bark,

- or on identification of some "marker substances", characteristic for the birch (bark) like betulin and/or other terpenes.

In all cases the problem dealt with was the differentiation b i r c h (*betula*) versus other trees, while the assertion p i t c h was never questioned.

Indeed one might have assumed — erroneously — that in the course of charcoal production for prehistoric metallurgical processes tars were obtained as by-products, which on heating yielded the pitches in question. The mistake in such assumptions became additionally obvious, when such dark organic materials were also found in stone age sites, even in ones dated as Palaeolithic.[6]

The consequence: *this material was not a by-product, but obviously the main target of a prehistoric technology.*

Although we also believed (and published) that the material in question is a p i t c h prepared from the bark of the birch, we nevertheless wanted to rule out the following alternatives:

Alternative 1: As it is known that betulin is somewhat soluble in acetic acid it could be possible that birch bark might have been simply extracted with a vinegar-containing liquid (simply accessible from some alcoholic liquid, obtained enzymatically from fruits). The extracted liquid could have been converted into the adhesive in question by drying up and heating.

Alternative 2: When hurting a birch in springtime a sap can be collected, which is said even to be used as a beverage in some regions. Once again it is conceivable that this sap on drying it up and on consecutive heating might yield the product in question, maybe also applicable as an adhesive.

What had to be done in order to rule out these possibilities was

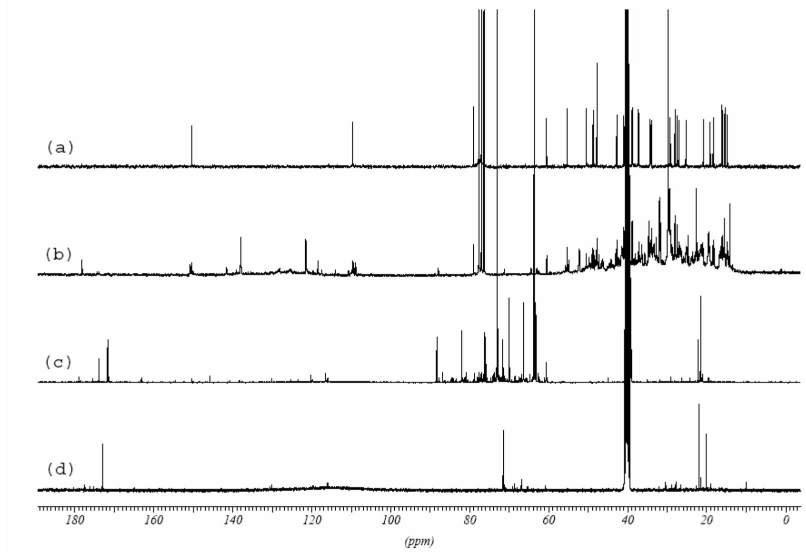
- to produce such materials,
- to find out whether or not such products can be used as adhesives, and
- to check whether or not the analytical results of such products could be confused with those of birch bark pitch

As described below (c.f. Experimental) the aqueous solutions obtained from both "starting materials" were dried up and heated to 200 °C to produce a pitch-like material. Using an analytical method which we published recently[7,8] these products after work-up by distillation gave a tarry oil, which was analyzed by ^{13}C-nmr spectroscopy.

Results and Conclusions

Indeed the substances thus obtained looked as if they were pitches; they also proved to act as adhesives.

4. Analysis of the products in question. Samples of the black, pitch-like looking materials were distilled in a Kugelrohr under reduced pressure (12 min. heating up to 300 °C, 22–25 mbar) to isolate the characteristic terpenoid fractions. 40–60 mg of these materials were dissolved in $CDCl_3$ or DMSO-d_6 and studied by ^{13}C nmr spectroscopy (Bruker DRX400 FT nmr spectrometer, 5 mm inverse broadband probehead, 20000 to 40000 scans, shifts relative to TMS). The following overview shows ^{13}C nmr spectra of (a) pure betulin, (b) a birch bark pitch containing substantial amounts of betulin, (c) material produced from the vinegar extract, and (d) product from the birch sap.



It is clearly visible that the composition of both of the materials in question is totally different from the birch bark pitch: whereas the characteristic triterpenoid constituents of the pitch cause a large number of signals in the aliphatic region between 15 and 50 ppm, almost no signals of this type can be found in the spectra of the alternative materials. Especially the complete lack of betulin is evident on a detailed analysis. In contrast, the analyzed products consist mainly of some carbohydrate-type compounds and small molecules, both of them being completely absent in the birch bark pitch.

Experimental Section

1. Acidic extraction of birch bark. Commercial vinegar prepared from apples (~5% acetic acid) was diluted with water (1:1), poured over birch bark broken into small pieces, warmed to 75–80 °C and kept at room temperature for 4 days. After filtration the solution was allowed to dry up at room temperature: the residue (~4% of the weight of the bark) was an orange-coloured to brownish, plastic mass, which was used for further studies.

In order to rule out that constituents already present in commercial vinegar might distort the results, one more extraction was carried out with pure acetic acid, diluted with water to 2,5%: anticipating the results no remarkable differences were obtained.

2. Use of natural birch sap. 43 g of natural birch sap collected after hurting a birch tree by drilling (Lower Austria, beginning of April2000) were allowed to dry up at room temperature, yielding 0.5 g of a plastic, yellowish-brown residue,which was used for analytical purposes.

3. Conversion of the residues into a dark product by heating. In order to simulate possible stone-age techniques samples of the residues obtained from the acidic extractions were spread on a flat piece of wood, covered with a small, flat stone, left at room temperature over night and heated to 200 °C (10 min. from room temp. to 200°, 15 min. at 200°, slowly cooling down), converting the residues into dark, solid and brittle materials. Samples of these products were used for analytical purposes.

Summary

By means of both conceivable alternative methods (i.e. acidic extraction of birch bark or drying up the natural birch sap, in both cases ensued by heating to ca. 200 °C) indeed products were obtained, which not only looked as if they were pitches, but also showed some property as adhesive. But as the results of our method of analysis were totally different from those obtained from prehistoric samples as well as from laboratory-made birch bark pitches, both alternatives can be ruled out. Therefore the dark organic substances containing relatively large(!) quantities of betulin which are frequently excavated in prehistoric central and northern Europe can really be considered as birch bark pitch.

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