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SHORT REPORTS

PRESENCE AND ORIGIN OF VOLATILE TERPENES IN SUCCINITE*

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Key Word Index—Baltic Amber; α-pinene; borneol; pine resin.

Abstract—The composition of the volatile fraction of four pine resins has been studied before and after an 'ageing' process. Typical terpenes of Baltic Amber were detectable after this 'ageing' process.

INTRODUCTION

It is a widespread belief that Succinite (Baltic Amber) is an 'aged' or 'fossilized' resin of pines [1]. With one exception [2], this idea has dominated the research on the chemical composition of Amber. Succinite is a very complex mixture in which polymers predominate: the key to understanding its composition lies in the transformations which must occur during the ageing of the resin. Ingenious hypotheses have been formulated along this line [3] but the 'chemical history' of this fossil resin has not yet been written. Borneol and other volatile terpenes (isoborneol, fenchyl alcohol, cymenes) have been found, and their presence has been recognized as indicative of the Baltic origin of Amber samples [4]. In addition to IR spectroscopy [5], GLC of volatile components has been suggested as an analytical tool to distinguish between Baltic Amber and other fossil resins [4], a problem of interest in archaeological studies.

RESULTS AND DISCUSSION

Results of detailed GC–MS analysis of a Succinite sample and four pine resins (*P. strobus*, *P. halepensis*, *P. pinaster*, *P. pinea*) are reported in Table 1. Apparently, the nature of terpenes found in Amber argues against a pine origin for this fossil resin: in general typical volatile terpenes present in pine resins are pinenes and carenes [6], and three of the four resins studied contain α-pinene as the main component.

When these resins were heated at 110° for 30–60 days, the composition of their terpenes changed. The comparison between composition of volatiles in the resins before and after the 'ageing' process suggests (see Table 1) that pinene is converted into borneol, iso-borneol, fenchyl alcohol and cymene(s), i.e. typical terpenes of Amber. Moreover fenchyl alcohol, borneol and isoborneol are formed in a roughly constant ratio. In Amber the observed constancy of this ratio has been indicated as a useful criterion for identifying this fossil resin [4]: now this observation can easily be rationalized on the basis of the origin of these substances.

The interpretation of other data collected here is not so straightforward. Limonene appears to be converted into α-terpineol (see results related to *P. pinea*), but the latter may originate from the pinene(s) (see *P. strobus*). 'Aged' resins also contain γ-terpinene and terpinolene as transformation products of pinene(s), whereas Amber contains the closely related terpinenols. Assuming a common origin for all these monocyclic terpenes, the different temperature under which Amber is formed can easily explain this difference. All 'aged' resins contain cymene(s), possibly a mixture of *m*- and *p*-isomers, not separated in our GLC conditions. In contrast, *o*-cymene is present in Amber, along with the mixture (if it so) of *m*- and *p*-cymenes. If the *o*-isomer has the same origin in Amber, this difference may be due to the temperature under which our experiments have been carried out. In conclusion, our experiments suggest that Baltic Amber is derived from resin which contained, as main component(s), pinene(s); this is in agreement with the commonly accepted idea about the origin of this fossil resin.

EXPERIMENTAL

Resin samples were collected in the Botanic Garden (University of Rome). They were dry and dusty. The 'ageing' process was carried out as follows: 0.3–0.5 g of the crude sample were sealed under H_2O in glass vials and heated at

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* Dedicated to Professor L. Panizzi on the occasion of his 70th birthday.

Table 1. Compositions of volatile fractions of Amber and resins of four pine species

Plants	Natural resin	Aged resin
P. pinea	α-Pinene (11), limonene (80), α-terpineol (9)	Unidentified (16), limonene (35), terpinolene (10), α-terpineol (39)
P. strobus	α-Pinene (81), β-pinene (19)	Unidentified (8), camphene (6), limonene (15), *m*-,*p*-cymene (10), γ-terpinene (5), terpinolene (21), fenchyl alcohol (5), borneol (9), α-terpineol (20)
P. pinaster	α-Pinene (72), β-pinene (3)	Unidentified (3), camphene (4), limonene (11), *m*-,*p*-cymene (17), terpinolene (18), fenchyl alcohol (3), borneol (8), α-terpineol (15), unidentified (3), guaiene (5), longifolene (19)
P. halepensis	α-Pinene (95), camphene (5)	α-Pinene (11), camphene (45), limonene (8), *m*-,*p*-cymene (6), terpinolene (5), fenchyl alcohol (4), isoborneol (3), borneol (13), α-terpineol (5)
Amber	α-Pinene (3), camphene (6), terpinen-4-ol (2), *m*-,*p*-cymene (14), terpinen-1-ol (14), *o*-cymene (11), fenchyl alcohol (10), isoborneol (2), borneol (33), carvomenthone (5)	

110° in a oven for 30–60 days. Similar results were obtained when the resins were heated in the vials under N_2.

Isolation of volatiles. Finely divided amber or 'aged' resin (0.3–0.5 g) was stirred in C_6H_6–$CHCl_3$, 1:1 (20 ml) for 3 hr at room temp. The solution was filtered and most of the solvent was removed; the residue was steam-distilled and the distillate extracted with EtOAc. The solution was concd and examined by GLC.

GC–MS analyses. A Varian 1400 instrument was used under the following conditions: 3% OV-17 on Silanized Chrom G 80–100 mesh column; 2.74 m long at programmed temp. (6°/min) from 90 to 170°; helium flow rate, 30 ml/min. MS spectra were taken on an AEI MS-12, coupled with the gas chromatograph (Biemann separator).

REFERENCES

1. Langenheim, J. H. (1969) *Science* **163,** 1157.
2. Gough, L. J. and Mills, J. S. (1972) *Nature* **239,** 527.
3. Rottlaender, R. C. A. (1970) *Archaeometry* **12,** 35.
4. Nicoletti R. (1975) *Studi e ricerche sulla problematica dell'Ambra,* pp. 299–305. Consiglio Nazionale delle Ricerche, Roma.
5. Beck, C. W., Wilbur, E. Meret, S., Kossove, D. and Kermani, K. (1965) *Archaeometry* **8,** 96.
6. Simonsen, J. L. (1949) *Terpenes.* Vol. II, pp. 64–65, 105. Cambridge University Press.