

## On Chemical Composition of Baltic Amber\*)

by

Tadeusz URBAŃSKI, Tomasz GLINKA, Elżbieta WESOŁOWSKA

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**Summary.** Solvents extracted a number of low molecular weight compounds of aromatic and terpenoid character, including oxygenated terpenes, from Baltic amber. It is rationalized that these compounds exist in amber in the form of ingredients of EDA complexes.

Previous experiments [1] have shown that vigorously ground Baltic amber contains a small amount of  $\Delta^3$ -carene which can be extracted with a nonpolar solvent, such as *n*-hexane. This monoterpene was not detected in an unground sample when treated with the same solvent. Vigorous grinding also increased the intensity of ESR signal [1—3] and this fact led to a suggestion that  $\Delta^3$ -carene was formed as a result of a "mechanochemical" reaction.

In our present experiments we examined the solubility of amber in both a nonpolar and a polar solvent: *n*-hexane and tetrahydrofuran (THF), respectively. Some new information should now be added to our previous finding. THF was formerly used in the analysis of amber by Rotländer [4], Nicoletti [5] and Kotarski [6].

Our results are collected in the Table.

TABLE

Solubility of Baltic amber in tetrahydrofuran and *n*-hexane determined by the loss of weight by treating with cold or hot (boiling temperature) solvents (in %)

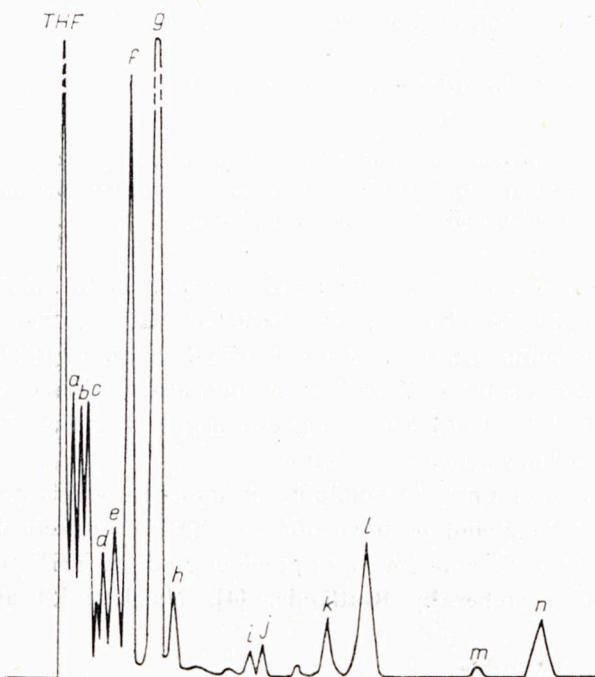
| Solvent | Pretreatment | Amber             |        |                  |        |       |        |
|---------|--------------|-------------------|--------|------------------|--------|-------|--------|
|         |              | light transparent |        | dark transparent |        | milky |        |
|         |              | THF               | hexane | THF              | hexane | THF   | hexane |
| Cold    | crushed      | 17.7              | 0.3    | 19.9             | 0.8    | 18.5  | 1.0    |
|         | powdered     | 21.2              | 2.4    | 18.5             | 1.1    | 21.9  | 5.7    |
| Hot     | crushed      | 17.1              | —*)    | 22.5             | 0.1    | 21.6  | —*)    |
|         | powdered     | 22.8              | 2.8    | 22.2             | 3.1    | 23.4  | 4.6    |

\*) Increase of weight through the absorption of the solvent.

\*) Contribution to the "Chemistry of Amber". Part IV.

A great difference was found between the quantity of the soluble matter extracted with these two solvents: THF dissolved 17.5—23.5% of the substance and *n*-hexane — 1.1—5.7%, deviations depending on the samples, their fineness and the temperature of extraction. The figures referred to THF are in agreement with the data obtained by Kotarski [6].

The fraction extracted with hexane was composed of volatile matter only, whereas the products extracted with THF contained only 10—20% of volatile substances, the rest being resinous products, presumably lower polymers of the abietic acid.



Gas chromatography dia-  
gram of volatile substances  
extracted with THF

- a* — a nonterpenoid hydrocarbon
- b* — terpenes m/e 136 and 140
- c* — terpenes m/e 136 and 138
- d* —  $\Delta^3$ -carene
- e* — 1,4-cineol (?)
- f* — 1,8-cineol
- g* — *p*-cymene
- h* — *o*- or *m*-cymene
- i* — pulegon (?)
- j* — a non terpenoid hydrocarbon
- p* — camphor
- l* — fenchénol
- m* — *iso*-borneol
- n* — borneol

The gas chromatography diagram of the volatile substances extracted with THF is given in the Figure, their compositions (in weight %) being as follows:

|                                |    |
|--------------------------------|----|
| <i>p</i> -cymene               | 49 |
| fenchénol                      | 10 |
| 1,8-cineol                     | 8  |
| borneol                        | 6  |
| camphor                        | 3  |
| $\Delta^3$ -carene             |    |
| 1,4-cineol (?)                 |    |
| <i>iso</i> -borneol            |    |
| pulegon (?)                    |    |
| <i>o</i> - or <i>m</i> -cymene |    |
| unidentified                   |    |
|                                | 24 |

Most of the substances were identified by comparing their retention peaks with those of the original samples. When this was impossible (due to the lack of standards) their assignment (based on mass spectrography only) is marked with an interrogation sign.

It is remarkable that the aromatic fraction of cumenes constitutes approximately half of the total quantity of volatile matters and the identified terpenes extracted with THF are (with the exception of  $\Delta^3$ -carene) oxygenated compounds (alcohols and ethers). To find out whether or not the oxygenated terpenes were formed through the oxidation of terpene hydrocarbons by trace peroxides which could be present in THF (although chromatographic grade was used), the extraction was repeated with a specially purified THF. The purification was carried out by distillation of THF over  $\text{Li}(\text{Al})\text{H}_4$ . No difference was found between the new results and those obtained previously.

With regard to the solubility of amber (Table) it was obvious to expect that the solubility of vigorously ground samples might be higher than that of only crushed samples owing to the development of the surface. However, it should not be excluded that a small proportion of monoterpenes, such as  $\Delta^3$ -carene, can be formed as a result of the "mechanochemical" breaking of the covalent C—C bond, as suggested previously [1, 2].

Since the aromatic compounds — cymenes — were found to be the main constituents of the volatile fraction, it should be pointed out that *p*-cymene is an ingredient of many essential oils found in coniferous trees [7].

A problem arises how cymenes and monoterpenes are combined in amber with its resinous substance and can be liberated: partly by mechanical action and mainly by acting with solvents.

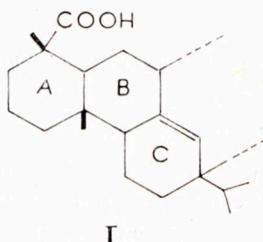
It is well known that on grinding amber evolves a definite terpene scent which is absent before grinding. This fact can partly be rationalized in terms of a covalent bond scission, as described previously [1, 2]. However, only a very small proportion of a monoterpenes can be detected in this way [2], and it seems possible to rationalize that the main body of lower molecular weight compounds are bonded with the polymeric substance, which is essentially the polyabietic acid, through the electron-donor-acceptor (EDA) phenomenon.

The hypothesis of the presence of EDA complexes in amber seems to be substantiated by the fact that amber gives a definite ESR signal, as reported previously [1—3]. It is well known that one of the characteristic features of EDA complexes is the presence of unpaired electrons, and the breaking of EDA complexes can occur under the action of suitable solvents.

Obviously, vigorous grinding combined with high temperature (produced through the friction) could also dissociate the "amber complexes" although according to the former experiments [2] the high temperature alone does not suffice to produce such an effect.

Another possibility is that clathrate complexes exist between the polyabietic acid and monoterpenes and aromatic hydrocarbons. The polyabietic acid should

be regarded as a host compound, coiled into a spiral, particularly if *cis*-decaline configuration of the *AB* rings of polyabietic acid (**I**) is accepted.



I

However, the existence of a clathrate complex cannot explain the presence of ESR signals given by amber. But the EDA complex could be combined with a clathrate structure and such a combination should give the ESR signal.

The fact that grinding increases the intensity of ESR signal [1, 2] indicates a typical behaviour of high polymers [8, 9]. Hence a conclusion can be drawn that the main body of amber is a high molecular weight polymer — polyabietic acid [2]. The insolubility of the polymeric substance in such a good solvent as THF should also support this view. The diabietic acid, suggested by Rottländer [4] to be the main constituent of amber, can of course be present in amber, but not as its main constituent.

### Experimental

Gas chromatography was carried out on a Varian AG 2868 apparatus, provided with a C-20-M column 10% on Chrom WAW/DMCS 80—100 mesh.

The solvents, *n*-hexane and THF ("Australan", Vienna), were of chromatography grade.

The solutions were concentrated under reduced pressure and ca. 1  $\mu$ l was introduced into the column in the stream of nitrogen under 32 psi.

The temperature of the column was 110°, of the detector (FID) 350°.

Air and hydrogen were introduced at a rate of 450 and 30 ml/min, respectively, attenuation being equal to 4.

Mass spectrography was carried out on a gas chromatography mass spectrometer LKB (Sweden).

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INSTITUTE OF ORGANIC CHEMISTRY AND TECHNOLOGY, TECHNICAL UNIVERSITY, KOSZYKOWA 75, 06-662 WARSAW  
(INSTYTUT CHEMII I TECHNOLOGII ORGANICZNEJ, POLITECHNIKA WARSZAWSKA)

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Т. Урбаньски, Т. Глинка, Э. Весоловска, **О химическом составе балтийского янтаря**

**Содержание.** Растворители экстрагируют из балтийского янтаря некоторое количество летучих веществ небольшого молекулярного веса. Это ароматики и терпеноиды, в том числе окисленные терпены. Предлагается гипотезу, что эти вещества входят в состав янтаря, как компоненты комплексов с переносом заряда.