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Chemistry of Baltic Amber. Part VII*)

by

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Summary. Fossile resin—amber from the Baltic Sea—is composed of lower molecular weight volatile compounds (2–5%) and polymers. The former are: aromatic hydrocarbons (cymenes), monoterpenes and their oxygenated derivatives. They can be extracted with THF. The polymer is composed of a soluble (20–25%) and an insoluble (65–75%) fraction of the total mass of the resin. The insoluble polymer is rationalized as a cross-linked polyabietic acid. The soluble oligomer is composed of at least two substances with the molecular weight corresponding to three units of abietic acid. It has a ketonic group. The existing view that amber is an ester of diabietinolic acid could not be substantiated.

It is well known that amber, the fossile resin originated from coniferous, has attracted attention of scientists mainly thanks to its remarkable property of charging with electricity on friction. The monograph on amber [1] and the review articles [2] appeared recently. They mention an early work by Unverdorben (1827), Berzelius (1828), M. Berthelot (1860) [1, 2].

A number of analytical work were carried out in the 19th and the beginning of the 20th c. but did not bring much information as regards its chemical structure until Tschirch *et al.* [3] pointed out a probable relation of amber to abietic acid and established that the fraction of amber insoluble in organic solvents ("succinoresen" according to their nomenclature) constitutes ca. 65% of the substance. The analysis of succinoresen corresponds to the formula $C_{22}H_{36}O_2$. It remained unchanged on boiling with aqueous 1% NaOH.

Schmid *et al.* [4] brought more information by their work on dehydrogenation of the soluble fraction of amber. Among the products they obtained

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*) Part VI. T. Urbański, Bull. Pol. Ac.: Chem., **25**, 785 (1977).

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pimanthrene (1,7-dimethylphenanthrene) and thus confirmed the view on the relation of amber to diterpenes. On the basis of infra-red spectra Beck *et al.* [5] considered that only a part of amber is an ester contrary to Rottländer [6] who came to the conclusion (through the formation of a number of model compounds) that amber is the polyester of diabietinolic acid. A number of authors [7–9] found that a considerable part of amber (15–25%) is soluble in aprotic solvents such as tetrahydrofurane. According to one of the authors of the present paper [9] the soluble part is composed of 2–5% volatile products, the rest being a resinous oligomer of a relatively low molecular weight which will now be called Polymer *S*. The volatile part contains monoterpenes (e.g. Δ^3-carene), monoterpene alcohols (fenchenol, borneol, iso-borneol, 1,8- and 1,4-cineols), ketones (camphor, pulegon), aromatic hydrocarbons present in essential oils (*o*-, *m*- and *p*-cymenes), and some terpenoid and non-terpenoid hydrocarbons difficult to identify. Particularly important is the presence of cymenes. They contain iso-propylic group, characteristic of abietic acid. All the volatile components seem to be absorbed by the polymer in the manner typical of polymers, similar to clathrates where the polymer forms a cage. A possibility of the CT effect should not be excluded considering that abietic acid building the polymer contains the carboxylic group—an electron acceptor—and amber shows a relatively strong e.s.r. signal of the intensity diminishing after the lower molecular weight fractions were extracted.

Some monoterpenes, such as Δ^3-carene, can be formed through the degradation of amber by mechanical action [10].

Mass spectrum of amber gives a relatively strong signal of m/e = 302 which can correspond to abietic acid [11].

The insoluble part isolated by the author of the present paper—polymer *A*—forms 65–70% of the total mass of amber. It appears to be a homogeneous substance and is probably identical with succinoresen of Tschirch [3].

In view of the fact that amber is a complex mixture, a number of papers dedicated to elemental analysis of amber [11–16] could not give conclusive results. To some extent the same applies to numerous data on IR spectra [14, 16–24], although some of these papers played an important part in elucidating the presence of some functional groups in amber and establishing geographical origin of amber. Thus Hummel [18] was the first to draw attention to the presence of bands typical of esters of succinic acid.

The thin layer [25] and gas chromatography [26] confirmed the multi-component system of amber. Early X-ray analysis [27, 28] showed that amber is amorphous, but more recent examination [29] established the presence of some crystalline components. Mass spectrographic examination [10, 30] did not reveal any information on the molecular weight of the polymeric part of amber. An important step to the chemistry of amber was its examination by proton magnetic resonance. All samples of amber show strong e.s.r.

signals. This was revelated by Lagercrantz and Yhland [31] and confirmed later by a number of authors [14, 16, 32].

Beck [33] examined NMR of soluble fractions of amber and found that they differ from abietic and diabietic acid and colophony. He also examined [34] soluble pyrolisates of amber and of pine resins and found that pyrolisate of Baltic amber contains significantly less *p*-cymene than that of modern pine resin and came to the conclusion that abietate structures are only a minor component of the fossil resin. This is contrary to our finding that nearly 50% of the volatile fraction of amber is composed of *p*-cymene [9]. We also could not find succinic esters and this is in agreement with some authors: the succinates were absent in their samples of amber [26, 35].

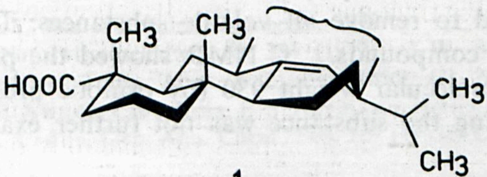
According to some authors (e.g. Helm [12], Klebs [13], Plonait [35] and others (see [1]) succinic acid present in amber is the result of "contamination" of essential oils by juices from plant cells and should not be regarded as a constituent of amber.

Results and discussion

The present study was dedicated to elucidating the structure of the main constituent of amber, i.e. the polymer insoluble in THF—Polymer *A*.

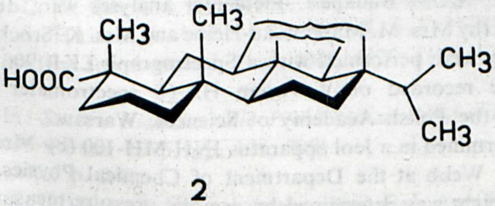
Polymer A. It is the most characteristic component of amber. It does not vary from one sample of amber to another and it confers mechanical properties of amber.

It is now rationalized that polymeric insoluble substance of amber—Polymer *A* is polyabietic acid (**1**) mainly in the cross-linked form (**2**). The analysis corresponds to abietic and polyabietic acid $C_{20}H_{30}O_2$ and excludes that of polydiabietinolic ester $C_{39}H_{58}O_2$ of Rottländer [6].



1

Abietic Acid polymer



2

Abietic Acid cross-linked polymer

It possesses characteristics of a cross-linked polymer: it is insoluble in all nonpolar and polar solvents, it shows a very high m.p. (620 C) and decomposition without melting at 490 C in the atmosphere of nitrogen and air, respectively.

It gives the IR spectrum typical of polymers with a very limited number of peaks. The most characteristic are those related to carboxylic group: 1730 and 1670 cm^{-1} from COOH free and hydrogen bonded respectively, a broad band at 3180 cm^{-1} of the OH group of COOH and hydrogen bonded. No bands related to double bonds could be detected and this agrees with the fact that catalytic hydrogenation and bromination indicated less than 1% of form **1**.

The important findings are bands: 1445, 1150 and 850 cm^{-1} which should be assigned to isopropylic group present in abietic acid.

Owing to its insolubility no ^1H NMR and ^{13}C NMR of polymer *A* could be taken and a chromatography be made. It was attempted to obtain soluble products by hydrolyzing the polymer. Boiling with aqueous 1% NaOH did not produce degradation, i.e. in agreement with finding of Tschirch [3] with one correction: the analysis indicated the formation of the semihydrate $C_{20}H_{30}O_2 \cdot 1/2H_2O$. The presence of water in the molecule was confirmed by IR spectroscopy.

It is known that a few diterpenic acids with isopropylic group can be transformed at 100 C in the sequence:

pimaric – neo-abietic – palustric – abietic acid [36].

Considering that abietic acid is the most stable of diterpenic acids with isopropylic group it is now rationalized that polymer *A* is a polyabietic acid (**1**) mainly cross-linked (**2**) and thus insoluble in any organic solvent.

The soluble fraction of the polymer. The fraction of amber dissolved in THF was evaporated to remove all volatile substances. The TLC indicated the presence of two compounds. ^{13}C NMR showed the presence of ketonic groups. It has the molecular weight 930 (by osmotic pressure).

For the time being the substance was not further examined.

Experimental

Baltic amber, light yellow, transparent washed with water was dried in a desiccator and powdered. M.ps. and decomposition temperatures were taken with a scanning calorimeter—Derivatograph, OD 102, MOM Budapest. Elemental analyses were done in a Perkin–Elmer 240 automatic apparatus (by Mrs. M. Majkowska-Heine and Mrs. K. Stocka). Mass spectrography and gas chromatography were performed with a Spectrograph LKB 900 (by Miss E. Malicka). ^1H NMR spectra were recorded on a Varian HA-60 spectrometer in $CDCl_3$ with TMS as internal standard at the Polish Academy of Sciences, Warsaw.

^{13}C NMR were determined in a Jeol apparatus JNH-MH-100 (by Mrs. H. Adamowicz-Brejt) and by Dr. Graham A. Webb at the Department of Chemical Physics, University of Surrey, Guildford. Molecular weight was determined by osmotic pressure measurement with a Hewlett-

-Packard 202 B osmometer and IR spectra recorded on a UR 10, Carl Zeiss, Jena in KBr and Nujol (by Miss M. Bułynko).

Polymer A [1, 2]. Amber (10.2 g) was refluxed for 4 h with THF (50 ml), the solution was removed by filtration. The operation was repeated four times. THF used for the extraction was freed of peroxides by distillation over $LiAlH_4$. The undissolved part—Polymer *A*—was dried *in vacuo* at room temperature. The yield was 6.4 g (62.75%).
Found: C, 79.65; H, 9.7, Calc. for $C_{20}H_{30}O_2$: C, 79.5; H, 9.9%.
Double bonds C=C by hydrogenation over Pt: 0.7; calc. for (**1**) 100, for (**2**)—0%. **IR**: 3450, 2940, 1730, 1670, 1455, 1365, 1235, 1150, 985, 895, 850 cm^{-1}.

Hydrolysis of polymer A with aqueous 1% NaOH. Polymer *A* (0.165 g) was refluxed with 1% solution of NaOH (5 ml) for 3 h. The insoluble substance was washed with water and dried *in vacuo* at room temperature. It did not show the change of the mass: a small dissolved portion was compensated by acquiring half a molecule of water.
Found: C, 77.2; H, 10.1; Calc. for $C_{20}H_{30}O_2 \cdot 1/2H_2O$: C, 77.2; H, 9.7%.
IR spectrum showed a broad band of water at 3100 cm^{-1} absent in polymer *A*.

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Т. Урбаньски, В. Моляк, **Химия балтийского янтаря**

Янтарь — ископаемая скала из Балтийского Моря состоит из летучих компонентов ниского молекулярного веса (2–5%) и полимеров. Полимеры состоят из растворимой фракции (20–25%) и нерастворимой (65–75%). Нерастворимая часть это полимер абетимовой кислоты с поперечными овязами. Растворимый олигомер состоит из трёх молекул абетиновой кислоты и содержит кетоновую группу.