THE QUESTION OF THE CHEMICAL STRUCTURE OF AMBER

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There are comparatively few papers [1–7] on the chemical study of amber, a natural fossil resin. We have continued these investigations.

The present paper gives the results of a comparison of the IR spectra and elementary compositions of various types of amber and natural resins related to amber but differing from the latter in age, and also those of its individual fractions.

Experimental

Baltic ambers were used as the subject of the investigation. The IR spectra were taken on an IKS-14 spectrophotometer with an NaCl prism in the 700–2000 cm^{-1} region. To determine the IR spectra, powder samples were prepared in the form of mulls in paraffin oil.

A comparison of the IR spectra of transparent, semitransparent, opaque, and bone ambers showed great similarity in the absorption curves, as has been reported previously [5–7].

Table 1

Analysis of Some Different Forms of Amber

Amber	Content, % of the organic fraction			Ash, %
	C	H	O (by difference)	
Transparent	81.57	10.50	7.93	1.33
Semi-transparent	78.41	10.57	11.02	None
Opaque	76.75	10.40	12.85	
Bone	80.04	9.99	9.97	

In contradistinction to the results of IR spectroscopy, the elemental analyses for the types of amber mentioned showed considerable differences (Table 1). Consequently, in this case it is more sensitive to changes in chemical composition. For subsequent investigations we took pine rosin (R) an amber-like resin (AR), amber (A), the oxidized skin from a piece of amber (S) and, as model substance, abietic acid (AA). The amber-like Urals resin readily dissolves in organic solvents (no amber is found in the Urals). Resins of this type are considered as "immature ambers"; their slow conversion into real ambers is favored by a reducing medium [8].

The IR spectra of the substances under consideration (Fig. 1) show that the amber-like resin is present, as it were, in a transition state, from a modern resin (of the type of rosin) to a fossil resin, amber. Thus, for AR and particularly for A the region of carbonyl absorption is broadened as compared with rosin and is deepened to about 1720 cm^{-1}. This shows a reaction at the carboxy group which has taken place slightly in the amber-like resin and to a greater extent in amber.

As the resins "age" (on passing from R to S), a displacement of the double-bond absorption band towards the short-wave region is found. For example, whereas in rosin the double-bond absorption is found at about 1630 cm^{-1}, in the amber-like resin it is at about 1640 cm^{-1} and in amber at 1654 cm^{-1} which possibly shows a change of conjugated double bonds into isolated double bonds on polymerization and isomerization. Moreover, the spectrum of AR shows appreciable absorption in the 791 cm^{-1} region which is considerably more intense in abietic acid and is absent in amber. This absorption band may be assigned to the characteristic frequency of a conjugated double bond in the neighborhood of the rings of a hydrophenanthrene system [9].

The IR spectrum of the crust (skin) of amber is similar to the spectra of the ambers. The authors of a recently published paper [10] came to the same conclusion. However, in a more detailed comparison of the spectra a still more pronounced increase in the intensity of the band at about 1720 cm^{-1} (which approximates to the intensity of the absorption of the COOH group) is found in the spectrum of the amber "skin" and an absorption at 1740 cm^{-1} which is masked in amber not separated into fractions clearly appears. Moreover, the double-bond band appears more sharply and a well-defined band at 1016 cm^{-1}, which may be assigned to the stretching vibration of C–O in acids, alcohols, ethers, and esters, is particularly enhanced.

It is possible that the appearance and deepening of the band in the 1720–1740 cm^{-1} region as the resins age is associated with the formation of lactones or esters [11, 12], this being preceded by the oxidation of the resin acids. The processes mentioned are difficult to detect by means of elemental analysis, since on oxidation and subsequent lactonization the composition of the resin changes only slightly. The comparatively ready oxidizability of resin acids with their subsequent cyclization under definite conditions to lactones is known also for the resin acids of rosin in acid media [7].

The separation of amber into fractions was carried out by the scheme due to Tschirch and Schmid, modified in part by ourselves. The proposed variant of the method is shown in the scheme shown on page .

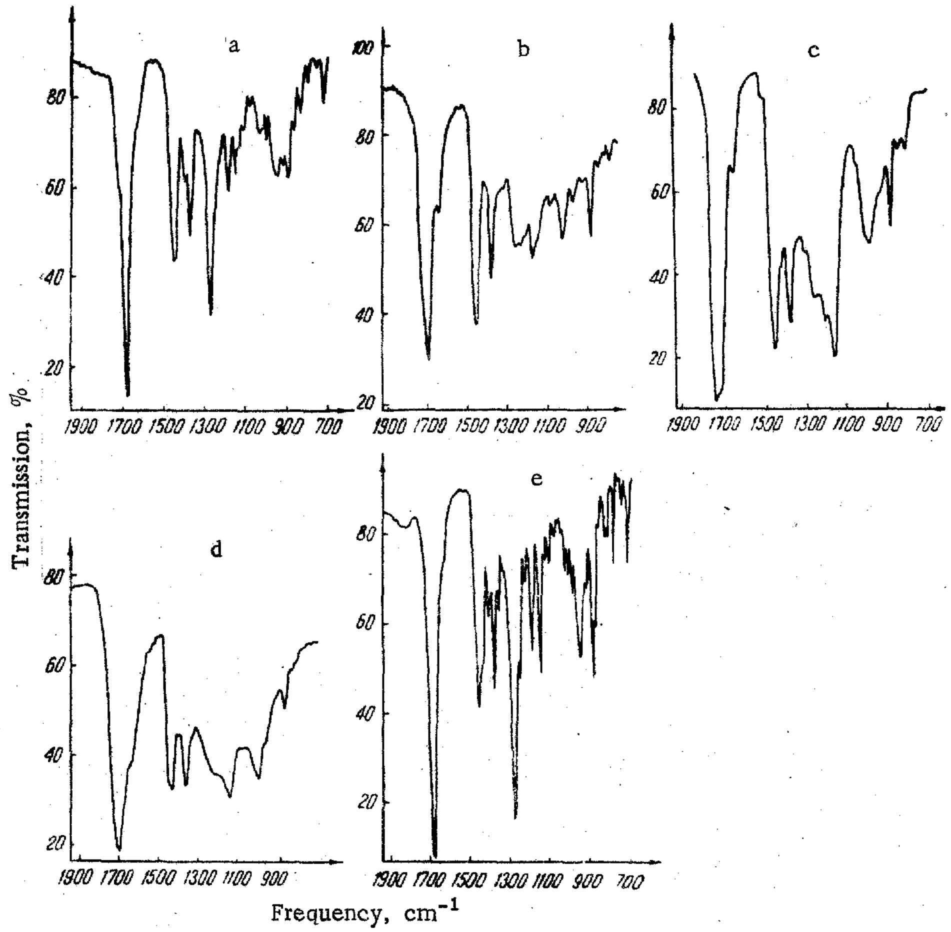


Fig. 1. IR absorption spectra. a) Pine oleoresin rosin, R; b) amber-like resin, AR; c) bone amber, A; d) oxidized skin of amber, S; e) abietic acid, AA.

The extraction of amber with cold alcohol was carried on for more than four months until the sample completely ceased to dissolve, and the residue was then boiled with alcohol in a Soxhlet apparatus for 213 hr. In view of the similarity of the IR spectra of fractions I and IIa (see scheme), the two fractions were mixed.

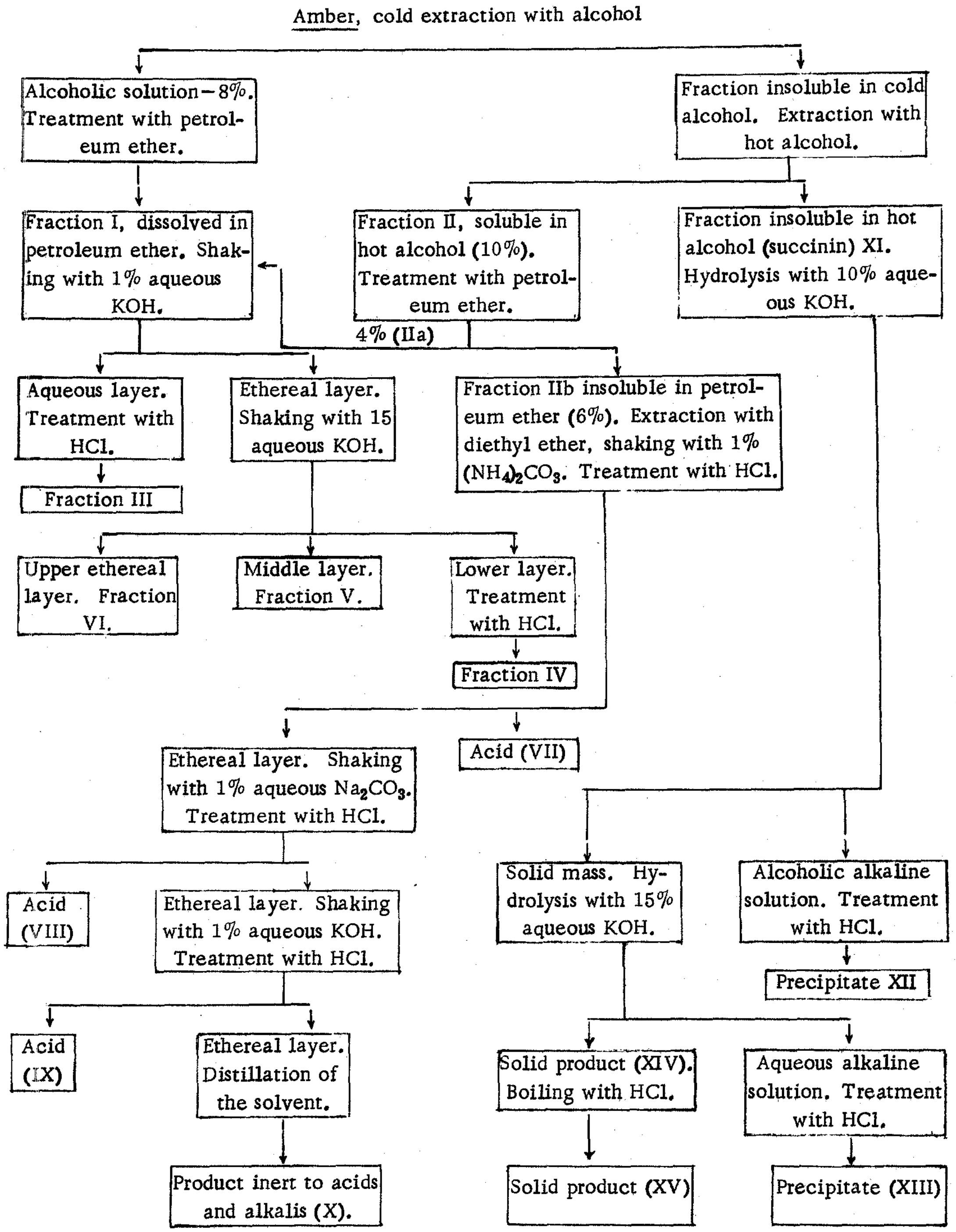
The IR spectrum of the amber fraction soluble in alcohol and in petroleum ether (Fig. 2, I) shows that it contains a large amount of acids (strong absorption bands at 1696 and 1274 cm^{-1}) and esters or lactones (strong bands at 1740 cm^{-1}) and also, apparently, resin alcohols or C—O groups in esters (1018 cm^{-1}).

Consequently, we considered that it was sufficient to shake the petroleum ether solution vigorously with aqueous solutions of alkalies of different strengths. In this way, we isolated fraction III in an amount of approximately 65% of the initial material. The IR spectrum of this (Fig. 2, III) showed a strong absorption band at 1689 cm^{-1}; however, on the shoulder of this line there is a broadening in the direction of higher frequencies which shows the presence of a certain amount (considerably less than on treatment with 1% KOH) of functional groups of the ester or lactone type. In addition, the spectrum of fraction III has the band of a double bond at 1635 cm^{-1}.

Fraction IV amounted to about 5% of the initial material. Its IR spectrum was very similar to that of Fraction III. The middle layer of fraction V had an intense orange color and the consistency of a viscous oil. The IR spectrum of the solid product isolated from this layer (Fig. 2, V) fairly clearly showed the presence of salts of acids, since it had strong bands at 1540 and about 1400 cm^{-1} which are highly characteristic for an ionized carboxy group. About 8% of ash was found in the product by quantitative analysis.

From the upper straw-yellow ethereal solution we isolated a product (VI) in an amount of about 17% of the initial material. The IR spectrum of this product showed the absence of free carboxy groups. A narrow intense absorption band at 1733 cm^{-1} indicates the presence of ester (or lactone) groupings in product (VI). Thus, the caustic alkali treatment of the given fraction of amber enabled us clearly to isolate groups of resinous substances (acid and ester fractions). The part

Scheme


Amber, cold extraction with alcohol
Alcoholic solution – 8%. Treatment with petroleum ether.
Fraction insoluble in cold alcohol. Extraction with hot alcohol.
Fraction I, dissolved in petroleum ether. Shaking with 1% aqueous KOH.
Fraction II, soluble in hot alcohol (10%). Treatment with petroleum ether.
Fraction insoluble in hot alcohol (succinin) XI. Hydrolysis with 10% aqueous KOH.
4% (IIa)
Aqueous layer. Treatment with HCl.
Ethereal layer. Shaking with 15 aqueous KOH.
Fraction IIb insoluble in petroleum ether (6%). Extraction with diethyl ether, shaking with 1% (NH4)2CO3. Treatment with HCl.
Fraction III
Upper ethereal layer. Fraction VI.
Middle layer. Fraction V.
Lower layer. Treatment with HCl.
Fraction IV
Ethereal layer. Shaking with 1% aqueous Na2CO3. Treatment with HCl.
Acid (VII)
Solid mass. Hydrolysis with 15% aqueous KOH.
Alcoholic alkaline solution. Treatment with HCl.
Acid (VIII)
Ethereal layer. Shaking with 1% aqueous KOH. Treatment with HCl.
Precipitate XII
Acid (IX)
Ethereal layer. Distillation of the solvent.
Solid product (XIV). Boiling with HCl.
Aqueous alkaline solution. Treatment with HCl.
Product inert to acids and alkalis (X).
Solid product (XV)
Precipitate (XIII)

of the amber soluble in alcohol but insoluble in petroleum ether (IIb) (see scheme) was almost completely soluble in diethyl ether.

The acids isolated via the ammonium and sodium salts in approximately equal amounts had similar spectra (Fig. 3; one of three similar spectra is given). The most characteristic features in these spectra are the strong absorption bands of a free carboxy group at 1268 and 1700 cm^{-1}, while intense absorption at about 1730 cm^{-1} appears on a shoulder of the latter. It may be assumed that these acids contain not only a free carboxy group but also one bound in the form of a lactone or ester.

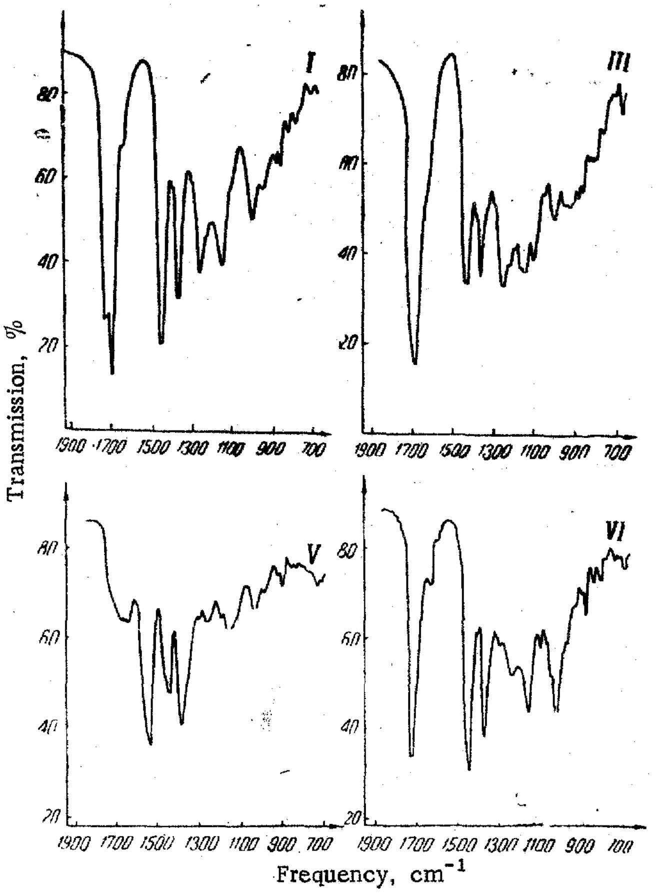


Fig. 2. IR spectra of fractions of amber soluble in alcohol and in petroleum ether. I) Product soluble in alcohol and petroleum ether; III) acids isolated by means of 1% KOH; V) potassium salts of the acids obtained by treatment with 15% KOH; VI) ester (lactone) fraction.

And, finally, more than 30% of the initial fraction remained as a brittle friable product inert to alkalis at room temperature (X). Its IR spectrum reproduces the main frequencies of the lines of the spectra of the preceding fractions (cf. Fig. 3) but differs in the ratio of the intensities. A considerable difference between products (VII)–(IX) is shown by their elemental analyses (Table 2).

Succinin (XI), i.e. the alcohol-insoluble fraction of amber, amounted to about 80% of the amount of transparent amber taken in our experiment. The IR spectrum of succinin (Fig. 4, XI) has a strong narrow absorption band at about 1730 cm^{-1} which is usually characteristic for esters and lactones without a strained ring and a clear absorption band for a double bond (1639 cm^{-1}). The spectrum of (XI) is very similar to that of product (VI). To further establish the structure of succinin, it was subjected to destructive hydrolysis by boiling with 10% alcoholic caustic potash for 74 hr. Even at the beginning of the hydrolysis, the whole mass acquired a dark yellow color and became very viscous and tacky.

After the completion of this stage of the hydrolysis, the residual mass was subjected to subsequent decomposition by boiling with 15% aqueous caustic potash for 20 hr (the subsequent treatment is shown in the Scheme).

The amount of precipitate (XII) was approximately 11% of the initial succinin, and the amount of (XIII) was about 2%. The IR spectra of products (XII) and (XIII) (see Fig. 4, XII) were identical and showed the presence of carboxy groups (1700 cm^{-1}), alcohol groups (1020 and 1094 cm^{-1}) and a double bond (1639 cm^{-1}).

The main product (XIV) remaining undissolved after hydrolysis amounted to about 98% (the total amount of product after hydrolysis must exceed the initial amount because of the addition of the elements of water). According to Tschirch and Schmid, the main product could be assigned to the unsaponifiable fraction, succinoresene. However, the IR spectrum (see Fig. 4, XIV) shows that in this case we have a salt of a hydroxy acid or a mixture of the salt of an acid with resinol. In favor of this is the appearance of strong absorption bands at 1550 and 1392 cm^{-1} [11]. A strong absorption band (which is absent in succinin) also appears in the 1023 cm^{-1} region, which shows the presence in this product of considerable amounts of alcohol groups. The absorption band at 1733 cm^{-1} characteristic for lactones (or esters) which is also present in succinin, disappears completely. The simultaneous presence of bands in the 1680–1695 and 1432 cm^{-1} regions, of which the band at about 1700 cm^{-1} does not have acid nature, may serve as an indication of the possible presence of a carbonyl group [11]; moreover, a strong band due to a double bond is found at 1634 cm^{-1}. The qualitative analysis of the product (XIV) showed the presence of a small percentage of ash.

These results permit the nature of products (XIV) to be defined as the salt of a hydroxyacid (or as a mixture of the salt of an acid and an alcohol). When the product (XIV) was treated with dilute hydrochloric acid, a substance with a high carbon content (XV) was obtained (cf. Table 2) with a yield of about 85% of the amount of (XIV).

As was to be expected, in the spectrum of succinoresene after treatment with hydrochloric acid (cf. Fig. 4, XV) the bands at 1551 and 1392 cm^{-1} had disappeared and a strong band at 1700 cm^{-1} had appeared, while the absorption band at 1020 cm^{-1} characteristic for an alcohol group had been retained.

In order to ascertain whether products (XIV) and (XV) contained a hydroxyacid (or its salt) or a mixture of an acid and an alcohol, product (XIV) was treated with boiling 50% aqueous alcohol in a Soxhlet apparatus for 4 days. However, it was impossible in this way to achieve the preferential dissolution of any possible component.

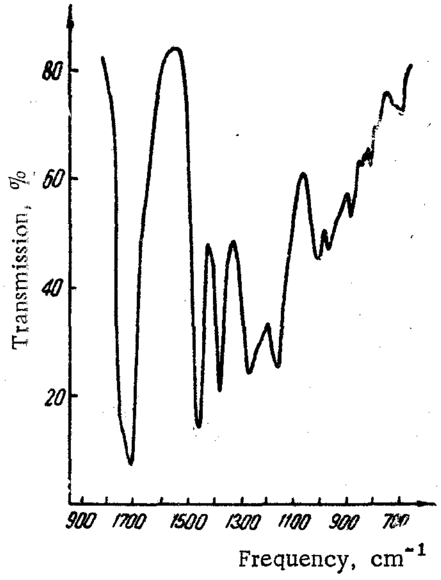


Fig. 3. IR spectra of some products from amber fractions soluble in alcohol and insoluble in petroleum ether. VII-VIII-IX (acids isolated by means of 1% solutions of $(NH_4)_2CO_3$, Na_2CO_3, and KOH.

Using the data of Tschirch and Schmid on the presence of considerable amounts of succinic acid in the alkaline hydrolyzate of succinin (2–70%), we determined it in the hydrolyzate of succinin by a known method [13]. Succinic acid was detected only qualitatively. The statement [14, 15] that amber consists to the extent of 70% of a succinic acid polyester is doubtful.

There is every reason for assuming that amber is a complex mixture (solid solution) consisting of lactones of oxidized resin acids and resin acids polymerized and bound to one another to different extents.

Summary

1. The identity of the IR spectra of the main types of amber (transparent, semitransparent, opaque and bone ambers) in the 700–2000 cm^{-1} region has been confirmed. At the same time, differences between them have been shown by elemental analysis.

2. In order to isolate the fraction of amber soluble in alcohol, extraction with boiling alcohol instead of by prolonged extraction at room temperature has been proposed.

Table 2

Composition of Individual Fractions of Amber

Product	Elemental composition, %			Empirical formula (calculated to C_{20})
	C	H	O (by difference)	
(VII)	76.88	9.85	13.27	$C_{20}H_{32}O_3$
(VIII)	79.08	10.22	10.70	$C_{20}H_{30}O_2$
(IX)	80.05	10.84	9.11	$C_{20}H_{32}O_{1-2}$
(X)	75.66	8.93	15.41	$C_{20}H_{28}O_3$
(XI)	80.00	10.43	9.57	$C_{20}H_{31}O_{1-2}$
(XV)	81.65	11.03	7.32	$C_{20}H_{32}O$

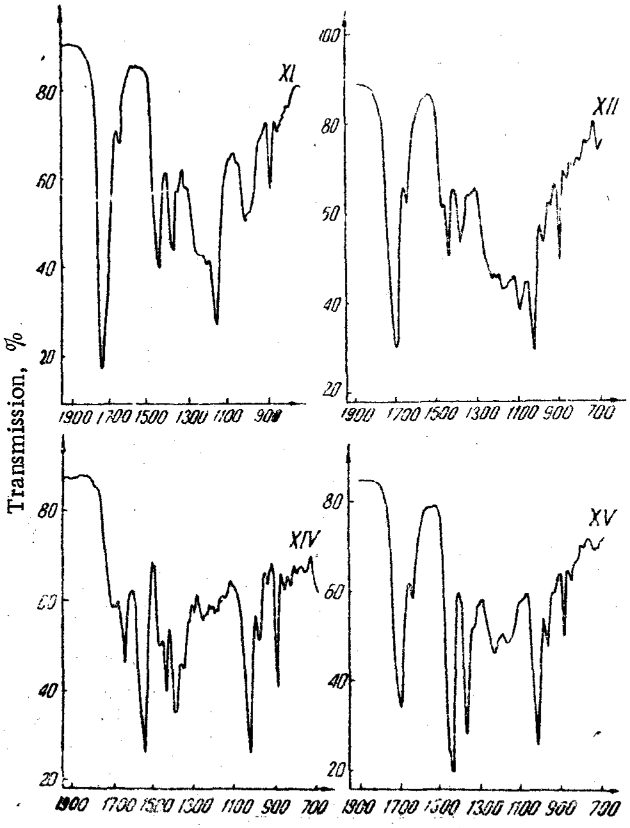


Fig. 4. IR spectrum of succinin and the products of its hydrolysis. XI) Succinin of transparent amber; XII-XIII) products isolated from the alkaline alcoholic and aqueous alcoholic solutions; XIV) main hydrolysis product (solid); XV) product XIV after treatment with HCl.

3. The amber fraction soluble in alcohol and petroleum ether can be separated into acid and ester (lactone) fractions by successive treatment of its ethereal solution with 1% and 15% aqueous alkalis.

4. The acid fraction isolated from the alcohol-soluble and the petroleum ether-insoluble fractions of amber have similar IR spectra but differ in elemental composition.

5. Succinin contains lactone (or ester) groupings whose hydrolysis forms hydroxyacids.

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