

THE ROLE OF ACID CATALYSIS IN THE GENESIS OF AMBER*

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Key Word Index—Baltic amber; fossil resins; hydrocarbons; 7,13-abietadiene; sclareol.

Abstract—Analysis of the hydrocarbon fraction from baltic amber is described. Transformations which have occurred in resins during the formation of amber are discussed on the grounds of acid-catalysed reactions undergone by 7,13-abietadiene and sclareol.

INTRODUCTION

The knowledge of the composition and the chemistry of succinite (baltic amber), a variety of fossil resin which can be identified by means of its IR spectrum [1, 2], is still poor, in spite of several studies [3] carried out during the last 150 years. Even the pine origin of the resin has been questioned [4]. Recently, we have shown [5] that the volatile components of amber [6] might be transformation products of the volatile compounds, i.e. pinenes and carenes, usually present in pine resins [7].

The idea that acid-catalysed transformations of terpenes have occurred during the formation of baltic amber has prompted us to study the nature of the hydrocarbons present in this fossilized resin.

RESULTS AND DISCUSSION

The benzene extract of baltic amber was worked up to remove the oxygenated compounds. TLC of the hydrocarbon part (less than 0.1% of amber), free from volatile components, gave four fractions (I–IV, numbered in order of decreasing polarity), each of which was examined by GC/MS. The MS data (M^+ and most important fragmentation ions of the hydrocarbons) are given in Table 1.

The most polar fraction (I) contained only one compound (1), identified as retene by comparison (MS, GLC) with an authentic sample. Fraction II contained two components (2 and 3). Compound 2 was identified as ionene (1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene) by comparison of its MS data with those reported in the literature [8]. The MS fragmentation pattern of 3, which was very similar to that of 2, suggested that it was a homologue of ionene.

Fraction III was a mixture of six major compounds (4–9). The compound (9) with the highest R_f was identified as dehydroabietane (by comparison of MS with that reported in the literature [9]). Fraction IV contained C_{15} and C_{20} hydrocarbons (10–23). Some of the GLC peaks given by this fraction contained more than one compound, as shown by the presence of two M^+ in the MS. They could not be separated however, even by using very efficient columns. This fraction also contained a compound (24) with the molecular formula $C_{22}H_{38}$.

The GC/MS analysis showed that baltic amber contains a very complex hydrocarbon mixture: the chain lengths of its components covering the range C_{13} – C_{22} . The general feature which derives from our analysis is that the hydrocarbons found in amber are mostly artefacts formed from the C_{15} and C_{20} terpenes originally present in the plant resin. The presence of retene, which is known to be a product of dehydrogenation of several diterpenes, is illustrative of this process.

The formation of aromatic structures and the presence of hydrocarbons with atypical numbers of chain lengths can be understood by considering two types of acid-promoted reactions: (1) hydride transfers, which, starting from cycloalkenes, leads to mixtures of aromatic and saturated compounds, (2) carbon–carbon cleavage and bond formation via carbonium ions. The hypothesis of acid-catalysed transformations was tested by GC/MS analyses of the less polar products generated by the acidic treatment (BF_3 and H_2SO_4) of a diterpene hydrocarbon (25; 7,13-abietadiene†) and a diterpene alcohol (26; sclareol). It was found that most of the GLC peaks were due to isomerizations of the starting materials. Nevertheless, some important observations were made. Treatment of 7,13-abietadiene with BF_3 furnished a hydrocarbon of MW 274 (2 μ more than 7,13-abietadiene) and another one of MW 284 (present also in the mixture generated by treating 25 with H_2SO_4), apparently due to the incorporation of a C_1 unit. More interestingly, we found a substance having a MS very similar to a

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†7,13-Abietadiene prepared following the method of Ruzicka and Waldmann [10] (see Experimental), is actually a mixture (GC/MS) of three substances: 7,13-abietadiene (25), which is the major component, dehydroabietane and a third compound with MW = 272.

Table 1. GC/MS spectral data for hydrocarbons 1–24 from baltic amber

TLC fraction, Compound*	[<i>m/z</i> (rel. int.)]	Important ions [<i>m/z</i> (rel. int.)]
Fraction I		
1 (C ₁₈ H ₁₈)retene	234 (64)	219(100), 204(40), 203(27), 202(23), 189(15)
Fraction II		
2 (C ₁₃ H ₁₈)ionene [8]	174	
3 (C ₁₄ H ₂₀)	188(16)	173(100), 158(10), 145(8), 143(8)
Fraction III		
4 (C ₁₄ H ₂₂)	190(14)	147(100), 133(10), 132(14), 119(40)
5 (C ₁₅ H ₂₂)	202(7)	159(100), 144(6), 131(8)
6 (C ₁₇ H ₂₄)	228(26)	185(35), 124(23), 109(54), 91(100), 81(67)
7 (C ₁₉ H ₂₈)	256(13)	241(70), 185(21), 159(100), 143(15)
8 (C ₂₀ H ₃₀)	270(2)	256(22), 241(87), 213(10), 185(26), 159(100)
9 (C ₂₀ H ₃₀)dehydroabietane [9]	270	
Fraction IV		
10 (C ₁₅ H ₂₄)	204(10)	189(22), 161(20), 148(54), 133(99), 107(100), 93(92)
11* (C ₁₅ H ₂₆ /C ₁₅ H ₂₄)	206(3)/204(3)	191(7), 189(3), 150(31), 134(100), 121(23), 107(48)
12 (C ₁₅ H ₂₄)	204(15)	189(8), 161(16), 148(60), 133(53), 119(28), 107(100)
13 (C ₁₅ H ₂₄)	204(2)	192(22), 177(34), 137(18), 121(21), 109(58), 95(100)
14* (C ₁₅ H ₂₆ /C ₁₅ H ₂₄)	206(5)/204(7)	192(15), 189(11), 177(33), 175(11), 109(76), 95(100)
15* (C ₁₅ H ₂₆ /C ₁₅ H ₂₄)	206(12)/204(7)	191(15), 189(4), 163(11), 161(10), 124(30), 109(100)
16* (C ₂₀ H ₃₄ /C ₂₀ H ₃₂)	274(3)/272(2)	232(37), 217(43), 109(81), 95(88), 81(95), 55(100)
17 (C ₂₀ H ₃₂)	272(2)	257(1), 245(3), 231(8), 137(75), 81(100)
18* (C ₂₀ H ₃₄ /C ₂₀ H ₃₂)	274(<1)/272(<1)	246(1), 231(5), 217(5), 163(10), 137(86), 81(100)
19* (C ₂₀ H ₃₄ /C ₂₀ H ₃₂)	274(<1)/272(<1)	259(1), 245(5), 230(6), 137(82), 81(100)
20 (C ₂₀ H ₃₂)	272(7)	258(27), 243(68), 161(67), 105(68), 95(68), 81(100)
21 (C ₂₀ H ₃₂)	272(3)	258(74), 245(50), 243(100), 137(43), 161(77), 105(91)
22 (C ₂₀ H ₃₂)	272(12)	257(25), 243(39), 231(51), 107(69), 95(83), 81(100)
23* (C ₂₀ H ₃₄ /C ₂₀ H ₃₂)	274(11)/272(8)	259(33), 245(44), 231(48), 163(87), 95(82), 81(100)
24 (C ₂₂ H ₃₈)	302(25)	287(92), 273(11), 259(13), 231(39), 205(71), 55(100)

*Compounds in each fraction arranged in order of increasing *RR*_r.

†Unresolved compounds.

component of the hydrocarbon mixture from amber (fraction III, compound 8) (Fig. 1). The analogy between the mixtures so obtained and the mixtures from amber can be easily seen. Acid treatment of sclareol gave a hydrocarbon which was identical with one derived from 7,13-abietadiene (Fig. 2). This fact showed that skeletal modifications are also possible. Therefore, discussions on the origin of amber, such as the one in ref. [4], which are based on the identification of certain substances with a particular carbon skeleton, cannot be conclusive.

The results described show that profound acid-catalysed transformations have occurred during the formation of amber. In this connection it should be stressed that the role of acid-catalysis in the genesis of amber has not been previously emphasized. As far as the polymeric nature of amber is concerned, the hypothesis that the polymer was formed by acid-catalysed polymerization of abietic acid is now under study.

EXPERIMENTAL

GC/MS: GLC: 3% Apiezon L on Chromosorb G (3-m column), He 30 ml/min temp. programmed 160–245° at 3.3°/min, injector and detector heater 250°; MS: AEI MS-12 instrument, 70 eV, Biemann separator.

Isolation and separation of hydrocarbons from baltic amber. 96 g baltic amber were ground to a fine powder and thoroughly extracted with hot C₆H₆ (2 × 400 ml). After the

removal of insol. residue by filtration, the solvent was distilled off through a 80-cm rectification column fitted with Fenske rings to give 9.1 g of a yellow oil. The oil was dissolved in Et₂O (500 ml) and washed with M Na₂CO₃ (4 × 100 ml). The organic layer was then dried over dry Na₂SO₄ and the solvent distilled off through the rectification column to give 4.6 g neutral components. The volatile components were stripped-off from a sample of 0.8 g by steam distillation, and the remaining aq. layer was extracted with Et₂O (3 × 30 ml). The combined organic extracts were dried over Na₂SO₄. Distillation of the solvent through a 20-cm Vigreux column afforded 0.69 g of high-boiling C₆H₆-soluble components. 0.4 g of this mixture was then subjected to prep. TLC (2 mm Si gel; C₆H₆–95% EtOH, 99:1). The least polar band was located (UV), and the hydrocarbons (10 mg) recovered (EtOAc) and rechromatographed TLC (0.25 mm Si gel; *n*-hexane). Four fractions (a strip of the plate was sprayed with 2 M H₂SO₄) were reversed (Et₂O) from the TLC plate and each was subjected to GC/MS.

Preparation of 7,13-abietadiene (25) [10]. **25** (2.6 g) was prepared from abietic acid (11.5 g) by methylation (CH₃N₂) followed by LiAlH₄ reduction of the ester followed by oxidation with K₂Cr₂O₇. The mp of the semicarbazone, after crystallization from MeOH, was 222–223° (uncorr.) (lit. mp 215° [10]). Spectroscopic analysis of the semicarbazone showed no impurities ¹H NMR (90 MHz, CDCl₃, TMS as int. standard): δ 8.83 [1H, *s*(*br*), lost on treatment with D₂O, –NH–], 6.77 (1H, *s*, –CH=N–), 5.75 (1H, *s*, –CH=C–CH=C–), 5.60–5.15 [3H, *br*; –CO–NH₂ and –CH=C–CH=C–; after

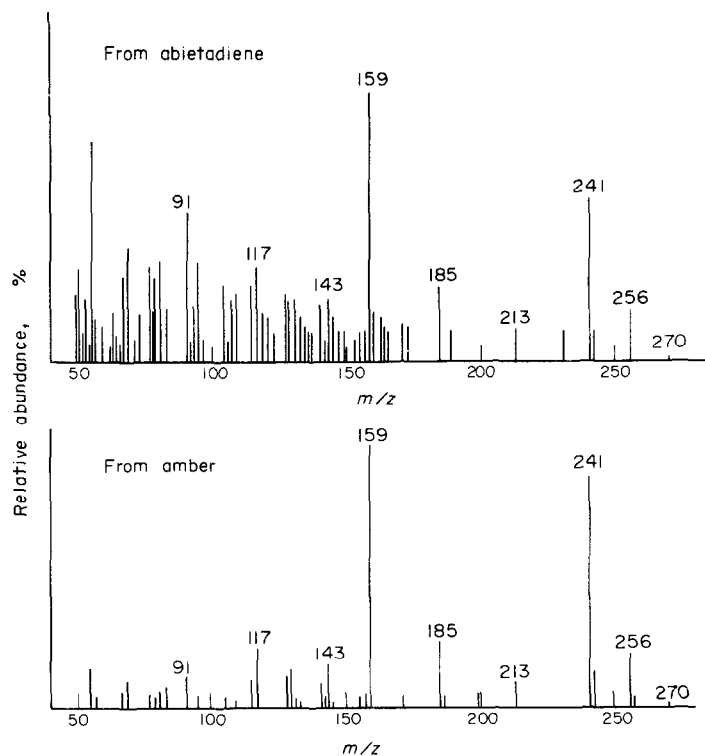


Fig. 1. Comparison between MS of component 8 and MS of a substance derived from treatment of abietadiene with BF_3 .

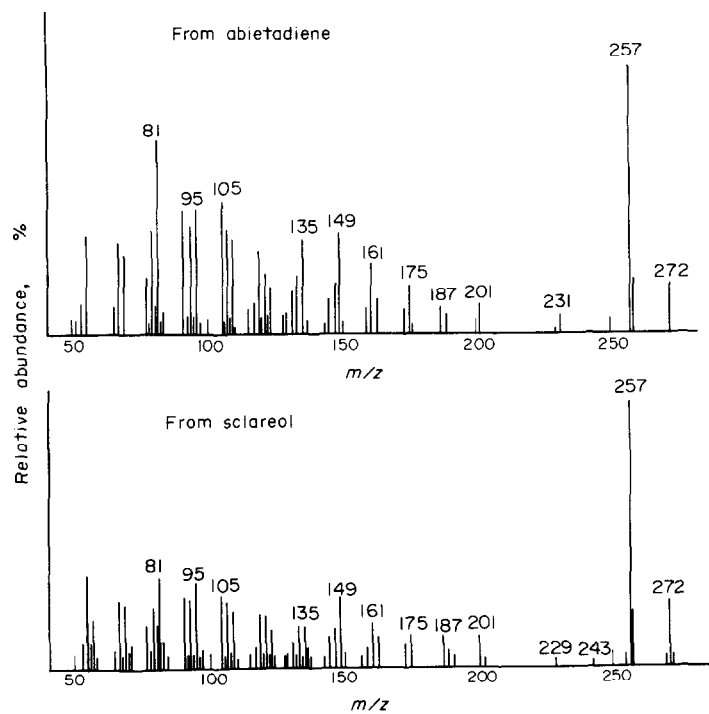
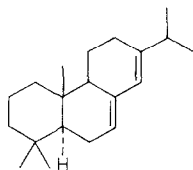
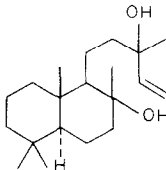


Fig. 2. Comparison between a substance derived from treatment of sclareol with BF_3 and a substance derived from treatment of abietadiene with BF_3 .

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treatment with D₂O only 1H, *s*(*br*) at 5.36], 1.1 (3H, *s*,

$\text{CH}_2\text{-C-CH=N-}$); 0.98 (6H, *d*, $J = 8$ Hz, *iso*-propyl); 0.82

(3H, *s*, angular Me). IR $\nu_{\text{max}}^{\text{neat}}$ cm⁻¹: 3450 (from 3550 to 2800), 1710, 1585. The semicarbazone of the aldehyde (100 mg) was heated for 1 hr, at 200–210° in diethylene glycol (1 ml) in the presence of powdered KOH (150 mg). The cooled soln was diluted with H₂O (10 ml) and thoroughly extracted with *n*-hexane. The organic layer was washed ($\times 3$) with H₂O and dried over Na₂SO₄. Evaporation of the solvent gave an oil (70 mg, one spot on TLC, *n*-hexane as eluant), which proved to be (GC/MS) a mixture of three components: 7,13-abietadiene (**25**) (80% by GC): MS m/z (rel. int.): 272 [M]⁺ (97), 257 (36), 255 (16), 229 (100), 187 (23), 173 (26), 159 (25); dehydroabietane [8]; a third compound with MW 272: MS m/z (rel. int.): 272 [M]⁺ (50), 258 (50), 257 (58), 243 (30), 215 (48), 187 (37), 161 (25), 159 (29). ¹H NMR (90 MHz, CDCl₃ with TMS as int. standard): δ 7.10–6.80 (arom.), 5.75 and 5.40 (olefinic), 1.22 (isopropyl group on a benzene ring, $J = 8$ Hz), 1.05–0.80 ($s \times 5$, Me groups).

Treatment of 7,13-abietadiene mixture with BF₃. 0.2 ml of 5% (w/v) 7,13-abietadiene in C₆H₁₂, containing 0.015 ml ethereal BF₃ (47%), was left at room temp. for 8 days in a sealed tube. The soln was then worked-up with a few drops

of satd NaHCO₃. The organic layer was dried over Na₂SO₄ and then directly analysed by GC/MS.

Treatment of 7,13-abietadiene mixture with H₂SO₄. 0.2 ml of 5% (w/v) 7,13-abietadiene in C₆H₆, containing 2 mg conc. H₂SO₄ was left at room temp. for 60 days in a sealed vial. After the usual work-up the mixture was analysed via GC/MS.

Treatment of sclareol (26) with BF₃. The treatment was similar to the one described for 7,13-abietadiene. The usual work-up gave an oil (10 mg) which was chromatographed on TLC (0.25 mm Si gel; *n*-hexane). A strip of the plate was sprayed with 2 M H₂SO₄ and the less polar fraction was recovered from the adsorbent with Et₂O and analysed by GC/MS.

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