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CORRELATIONS BETWEEN BALTIC AMBER AND *PINUS* RESINS

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Key Word Index—Baltic amber; *Pinus halepensis*; *P. pinea*; *P. pinaster*; *P. strobus*; Pinaceae; resins; acid fraction; retene.

Abstract—The composition of the acid fractions of four pine resins has been studied before and after an 'ageing' process. Correlations are established between Baltic amber and 'aged' *Pinus halepensis* resin.

INTRODUCTION

In previous papers [1, 2] we studied the transformations of volatile terpenes, present in some pine resins, occurring during an 'ageing' process. This process consisted of heating the resins at 110° for 30–60 days. The fossilization process that produces resins is not completely clear, but it probably involves oxidation and polymerization by a free-radical mechanism, which can be fastened by heat or light. According to our results, *Pinus halepensis* resin, after the 'ageing' process, gave products characteristic of Baltic amber (succinite), such as fenchyl alcohol and borneol, in a ratio similar to that found in amber. To explain the formation of such products we investigated the possibility that the resin medium acts as a liquid crystal [3]. Results obtained have shown that nematic and cholesteric media, whose orientational rigidity is very low, act as 'normal' isotropic solvents, while tightly ordered smectic solvents exert stereochemical effects, partly reflecting results obtained with resins as the reaction medium. The necessity for acid catalysis is confirmed by the stability of terpenes observed when the 'ageing' process is carried out in a non-protic solvent [3], while the sole effect of an acid medium as a driving force in monoterpene rearrangement has been studied without appreciable results [4].

The present paper describes the transformations of the acids contained in the resins of four pine species, *P. halepensis*, *P. pinea*, *P. pinaster* and *P. strobus*, which occur during the 'ageing' process. The aim was to establish, if possible, further correlations between pine resins and Baltic amber. Moreover, since retene has been found in samples of succinite [5], we have investigated its formation in the ether soluble extracts of the resins examined.

RESULTS AND DISCUSSION

The ether soluble acid fraction of Baltic amber and of the four pine resins were studied by GC/MS, before and after the 'ageing' process. The components of the acid fraction were identified by comparing their mass spectra with those in the literature [6] and were quantified by an internal standard method (Table 1). It has been previously reported [7] that the content and composition of resin acids in pine wood change with tree age. The process of transformation of the resin acids proceeds from the original acids to abietic acid [7], which is transformed into 'pyroabietic' acid. This can be dehydrogenated to dehydroabietic acid and decarboxylated to retene, or be reduced to tetrahydroabietic acid which is, subsequently, decarboxylated to fichtelite.

As shown in Table 1, Baltic amber contains a larger amount of dehydroabietic than of abietic acid and of 8,15-isopimaradien-18-oic than of 8,12-abietadien-18-oic acid. In *P. pinea*, *P. pinaster* and *P. strobus* the 'ageing' process produces a higher amount of abietic than of dehydroabietic acid, in agreement with published results [8]. For the same pine species the amount of 8,15-isopimaradien-18-oic acid, found after the 'ageing' process, is always lower than the amount present in the fresh resin, while the content of 8,12-abietadien-18-oic acid remains almost unchanged.

Transformations occurring in aged *P. halepensis* resin give rise to products similar to those found in Baltic amber. The amount of dehydroabietic acid rises to more than twice the abietic acid content, thus giving a dehydroabietic–abietic acid ratio in excellent agreement with that found in our samples of succinite and those quoted in the lit. [9]. Moreover, 8,15-isopimaradien-18-oic acid is present in fresh *P. halepensis* resin in amounts lower than those of 8,12-abietadien-18-oic acid, as is the case in the other examined resins. After the 'ageing' process, however, the former predominates greatly over the latter, as is the case in Baltic amber. The limited data available at present do not allow any explanation of the transformations occurring in succinite and in *P. halepensis* resin and are, therefore, reported simply as experimental evidence.

We have also investigated the possible formation of retene in aged resins. Retene, absent in fresh resins, has been detected in Baltic amber [5]. Retene could be detected only in aged *P. halepensis* resin. Abietic acid itself, aged with the same procedure used for resins, does not form retene.

The assignment of the source of Baltic amber to the genus *Pinus* was established by Schubert [10] and later confirmed by several authors [1, 11, 12]. Botanical evidence also supports this hypothesis, viz. the presence of

Table 1. Composition of acid fractions from amber and fresh and aged pine resins

Amber	Isopimarate	33%
	8,15-Isopimaradien-18-ate	20%
	8,12-Abietadien-18-ate	10%
	Dehydroabietate	21%
	Abietate	16%

Pine species	Fresh resin		Aged resin	
P. halepensis	8,15-Isopimaradien-18-ate	12%	8,15-Isopimaradien-18-ate	30%
	8,12-Abietadien-18-ate	20%	8,12-Abietadien-18-ate	12%
	Dehydroabietate	35%	Dehydroabietate	41%
	Abietate	33%	Abietate	17%
P. pinaster	Unidentified	4%	Unidentified	4%
	Pimarate	14%	Pimarate	12%
	8,15-Isopimaradien-18-ate	13%	8,15-Isopimardien-18-ate	4%
	8,12-Abietadien-18-ate	12%	8,12-Abietadien-18-ate	15%
	Dehydroabietate	27%	Dehydroabietate	26%
	Abietate	30%	Abietate	39%
P. pinea	Pimarate	10%	Pimarate	7%
	8,15-Isopimaradien-18-ate	7%	8,15-Isopimaradien-18-ate	4%
	8,12-Abietadien-18-ate	23%	8,12-Abietadien-18-ate	24%
	Dehydroabietate	23%	Dehydroabietate	28%
	Abietate	37%	Abietate	37%
P. strobus	8,15-Isopimaradien-18-ate	32%	8,15-Isopimaradien-18-ate	8%
	8,12-Abietadien-18-ate	35%	8,12-Abietadien-18-ate	36%
	Dehydroabietate	16%	Dehydroabietate	10%
	Abietate	17%	Abietate	46%

droplets of amber in the resin canals of wood of the pinaceous type and the occurrence in amber of pinaceous needles, female cones and male fructifications [13]. Only Gough and Mills [9], having found agathyc acid in a sample of succinite, has argued for some *Agathys* species resin as a botanical precursor, although no araucarian remains have been found in the Baltic area [13]. Some chemical correlations between resins of pine and of araucarian species have already been established [14], because of the isolation from *P. lambertiana* of lambertianic acid, which belongs to the same series as agathyc acid. Moreover, in fresh pine resins examined we found agathyc acid (1–3%). This can account for Gough's agathyc detection in Baltic amber and, in agreement with Schubert's results, suggests that Baltic amber might come from a kind of pine tree, or that pines of the Baltic area are derived from a common ancestor of both araucarians and pines [13].

The results described here (transformations of resin acids, retene formation) specifically suggest *P. halepensis* as a precursor of Baltic amber. Geological data can be found in support of this hypothesis. During the Paleocene and Oligocene periods the composition of soil in Baltic regions was mainly calcareous [15] and contemporary *P. halepensis* grows preferably on calcareous soil [16].

EXPERIMENTAL

Resin samples were collected in the Hortus Botanicus of the University of Rome, from trees aged 50 years. Abietic acid, from Merck, was re-crystallized twice from EtOH–H_2O. 'Ageing' was carried out as previously described [1].

Isolation of acid fraction. Fresh and aged resin, and finely divided amber were stirred in Et_2O for 2 hr. Solns were extracted twice with $NaHCO_3$, acidified and extracted with Et_2O. They were concd, esterified with CH_2N_2 and examined by GC/MS under the following conditions: Carbopack C + 2.5% PEG 20 M, 1 m column, at 230°, carrier gas H_2. MS: 70 eV, Biemann separator.

Identification of retene. The Et_2O solns, after extraction with $NaHCO_3$, were concd and examined by GC. Analytical conditions: 3% OV-17 on silanized Chromosorb G 80–100 mesh, 3 m column, at 230°, carrier gas He. Retene identity was confirmed by comparison of its R_t on an Apiezon L GC column with that of an authentic sample, previously synthesized.

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FOUR EUDESMANOLIDES FROM *MONTANOA FRUTESCENS**

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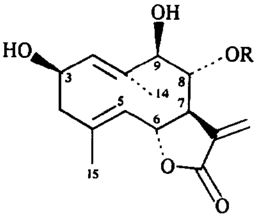
Key Word Index—*Montanoa frutescens*; Asteraceae; Heliantheae; eudesmanolides; sesquiterpene lactones.

Abstract—Chemical analysis of *Montanoa frutescens* afforded the known sesquiterpene lactones montafrusins A and B, as well as four new eudesmanolides which we have named montafrusins C, D, E and F. The structures of the new compounds were established by spectroscopic methods.

INTRODUCTION

As part of our continuing study on the chemistry of plants of the genus *Montanoa*, we have examined the sesquiterpene lactones of the Mexican species *M. frutescens* [1], *M. tomentosa* [2, 3] and *M. grandiflora* [4].

Recently we re-investigated *M. frutescens* and isolated, besides the already described montafrusins A (**1a**) and B (**1b**), four new eudesmanolides which we have named montafrusins C, D, E and F.



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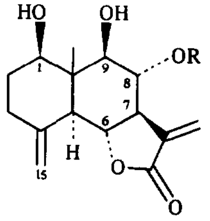

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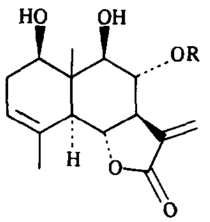

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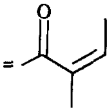

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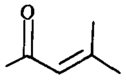

RESULTS AND DISCUSSION

Montafrusin C (**2a**), $C_{20}H_{26}O_6$, mp 140–144°, gave rise to two one-proton doublets at δ6.14 ($J = 3.0$ Hz) and 5.48 ($J = 3.0$ Hz) and IR absorption at 1750 cm^{-1} typical of an α,β-unsaturated γ-lactone. Further IR absorptions at 1715 and 3400 cm^{-1} indicated the presence of an α,β-unsaturated ester and hydroxyl groups. The unsaturated ester was shown to be an angelate on the basis of the diagnostic ^{1}H NMR absorptions at δ6.24, 2.05 and 1.95 due to the vinyl proton and methyl groups together with mass spectral peaks at m/z 83 and 55.

Detailed ^{1}H NMR spin-decoupling experiments allowed the major structural assignments of montafrusin C (**2a**). Irradiation of the triplet of triplets at δ2.91 (H-7)

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*Contribution No. 711 from Instituto de Química, UNAM, México.