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COMPARISON OF BALTIC AMBER AND AN 'AGED' *PINUS HALEPENSIS* RESIN BY MEANS OF INFRARED SPECTROSCOPY

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Key Word Index—*Pinus halepensis*; Pinaceae; resin; Baltic amber; infrared spectroscopy; terminal methylene; polymerization.

Abstract—The infrared spectrum of 'aged' *Pinus halepensis* resin indicates the presence of a methylene group in a terminal position, which is characteristic of Baltic amber.

INTRODUCTION

Earlier reports from this laboratory [1, 2] indicate correlations between Baltic amber and *Pinus halepensis* resin, 'aged' as described in ref. [1]. Infrared spectroscopy has long been used as an analytical tool to distinguish between recent and fossil resins and samples of amber of different origins [3-5]. Amber from Chipas, Mexico, has been successfully related to resin of *Hymenaea courbaril* by comparing their infrared spectra and amber from Sumatra has been related to *Shorea* sp. resin in the same way [3]. We have examined the infrared spectra of Baltic amber and of fresh and 'aged' resin from *Pinus halepensis* (Fig. 1).

RESULTS AND DISCUSSION

The interpretation of the infrared spectra of amber and similar resins is difficult because of the heterogeneity and complexity of these materials, which often lead to broad bands, further complicated by shoulders. Our assignments of bands are based upon the interpretation of Beck *et al.* [4].

Figure 1 shows infrared spectra of a Baltic amber and of fresh and 'aged' *Pinus halepensis* resin. Two absorption bands (at 885 and 1150 cm^{-1}) are characteristic of Baltic amber. The sharp band at 885 cm^{-1} has been attributed to the out-of-plane carbon-hydrogen bonding of a terminal olefin group. Rottländer [6] considered it a β-naphthalene-like structure. Among fossil resins, gedanite, neudorfite, euosmite and rumanite show this absorption band but not glessite, krantzite, duxite, ajkaite, walchowite, scraufite and the French 'pseudo-succinite' [4].

Fresh resin of *P. halepensis* does not absorb very characteristically in this spectral range, nor do resins of *P. pinea*, *P. pinaster* and *P. strobus*. 'Aged' *P. halepensis* resin, however, shows a sharp absorption band at about the same frequency (890 cm^{-1}) as Baltic amber (884.5 cm^{-1}). The difference in the absorption frequency may be a consequence of differences in chemical environment.

The spectral range between 1250 and 1100 cm^{-1} contains another absorption pattern characteristic of Baltic amber. It consists of a broad shoulder between 1250 and 1175 cm^{-1}, followed by a sharp absorption peak at 1150 cm^{-1}. This has been attributed to carbon-oxygen single bond stretchings of saturated aliphatic esters [4, 6]. The same absorption pattern is shown by the sample of Baltic amber examined by us (Fig. 1). Fresh pine resin

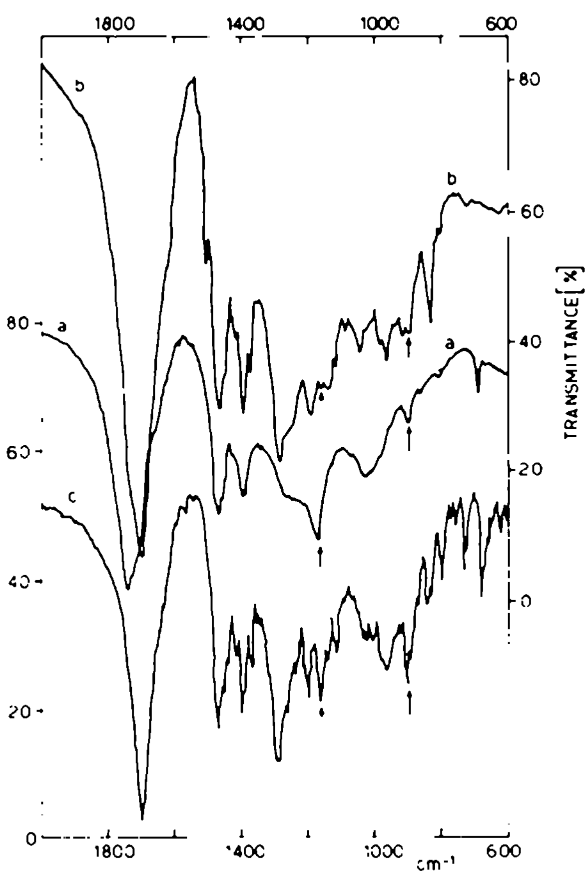

Fig. 1. Infrared spectrum in KBr pellets of (*a*) amber; (*b*) fresh *P. halepensis* resin; (*c*) 'aged' *P. halepensis* resin.

does not aborb significantly at $1150\,cm^{-1}$, but the 'aged' resin shows a three-band absorption (1250, 1205, $1150\,cm^{-1}$), typical of saturated aliphatic esters [7]. It also shows a sharp absorption band of high intensity at $1270\,cm^{-1}$, as does fresh resin, due to C–OH stretching of free carboxyl groups [6, 7].

Our results indicate that polymerization (formation of ester bonds) has started in our 'aged' *P. halepensis* resin, but it is still at its beginning (presence of free acid bonds). The formation of terminal olefinic double bonds has already taken place.

EXPERIMENTAL

Pinus halepensis resin was 'aged' for one year, under water, as in ref. [1], after separation of the volatile fraction by steam distillation. Spectra were recorded using an Infrared Spectrophotometer (FTIR) Bruker IFS 113 v. Samples were examined in KBr pellets.

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ESSENTIAL OIL COMPOSITION OF JUVENILE LEAVES FROM COPPICED *EUCALYPTUS NITENS*

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Key Word Index—*Eucalyptus nitens*; Myrtaceae; shining gum; juvenile foliage; essential oil; capillary column GC-MS.

Abstract—The essential oil of *Eucalyptus nitens* juvenile foliage harvested from coppiced trees contained α-pinene, limonene, 1,8-cineol, *cis*-ocimene and α-terpineol as principal components. Minor constituents were monoterpene alcohols, ketones, and aldehydes and 3-methylbutanal. Esters not previously identified in *E. nitens* leaf oil were ethyl 3-methylbutanoate, 3-methylbutyl-3-methylbutanoate, 3-methylbutyl hexanoate and hexyl 3-methylbutanoate.

INTRODUCTION

The possibility of *Eucalyptus* oil production [1] has been investigated in New Zealand forestry practice using a southern New South Wales provenance of *E. nitens* Maiden. This species has been reported to contain nearly 50% 1,8-cineol in the oil from the adult tree foliage [2]. However, when coppiced, *E. nitens* produces juvenile foliage having anatomy typical of that of seedlings, not of the adult tree. Only one investigation of the composition of the oil of a *Eucalyptus* seedling foliage has been described, that of *E. delegatensis* [3]. Recently, the essential oil composition of *E. delegatensis* foliage has been re-examined [4], and comparisons drawn between steam distillation and solvent extraction methods for essential oil isolation, particularly the formation of hydrocarbon artefacts arising from dehydration of labile alcohols with steam.

This report describes the content and composition of the oil from leaves from coppiced *E. nitens*.

RESULTS AND DISCUSSION

Using simple hydrodistillation, *E. nitens* juvenile foliage gave a very pale yellow oil, in 1% yield, or *ca* 4.3 kg