Phytochemistry, 1972, Vol. 11, pp. 1815 to 1818. Pergamon Press. Printed in England.

SHORT COMMUNICATION

EFFECT OF AIR POLLUTION ON THE VOLATILE OIL FROM LEAVES OF *PINUS PONDEROSA*

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(*Received* 9 *November* 1971)

Abstract—The composition of the essential oil from the leaves of photochemical air pollution injured and healthy *Pinus ponderosa* trees was determined. Methyl chavicol, a product of the carbohydrate-shikimic acid metabolism, was strikingly lower in the injured trees. However, no significant differences were observed in the monoterpenoids.

INTRODUCTION

STUDIES made in the San Bernardino Mountains of southern California have shown that *Pinus ponderosa* trees severely injured by photochemical air pollution became infested by the bark beetles, *Dendroctonus brevicomis* and *D. ponderosae*.[1] Pitch tubes produced by attacking beetles were more common on pollution injured trees than on more healthy trees even when the trees were not mass-attacked and did not succumb. Thus, the possibility exists that beetles are attracted to the injured trees. If such attraction occurs, it could be a response to differences in volatile compounds emitted by injured trees. Several investigators[2–4] showed that certain terpene alcohols act as pheromones of *D. brevicomis* and that natural terpene hydrocarbons enhance attraction of these compounds.[5] No significant differences in the proportion of terpenes in stem xylem of healthy and injured trees were detected in a study by Miller *et al.*[6] but the foliage, because of its exposure, may be a more logical source of attractive volatiles. The effect of photochemical air pollutants on the production and composition of volatile oils from foliage has been the subject of only a few studies. In Pinaceae, Cvrkal[7] working with the leaf oil of *Picea excelsa* L. reported a positive correlation of β-pinene and a negative correlation of camphene and limonene content with photochemical air pollution injury. In the present paper, the possible air pollutant—foliage oil—bark beetle relationship is examined by study of the essential oil composition of injured and healthy *Pinus ponderosa* trees from the San Bernardino Mountains near Los Angeles.

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RESULTS AND DISCUSSION

The composition of the essential oil from the foliage of central Sierra Nevada *Pinus ponderosa* has been the subject of our previous publication.[8] Although the composition of stem xylem monoterpenoids from the San Bernardino ponderosa pine has been reported to be markedly different from the Sierra Nevada material,[9] this was not the case with needle oil of this species with the possible exceptions of slightly lower 3-carene values and higher variabilities for α-pinene and methyl chavicol. The major part of the volatile material was represented by α- and β-pinene and methyl chavicol, with smaller amounts of 3-carene, myrcene, limonene, β-phellandrene and terpinolene—the latter in trace amounts (Table 1). As in our former study, the amounts of methyl chavicol and total monoterpenoids were expressed as percentage of the weight of the green foliage analysed, since the two constituents are formed by different biosynthetic paths. The percentage of individual monoterpenoids, arising presumably from the same nerylpyrophosphate intermediate, were expressed on the basis of their total.

TABLE 1. AVERAGE COMPOSITION OF THE NEEDLE OIL FROM HEALTHY AND DISEASED *Pinus ponderosa* TREES GROWING IN SAN BERNARDINO NATIONAL FOREST, COLLECTED MAY 1967

Constituent*	Healthy trees		Injured trees	
	Mean	S.D.	Mean	S.D.
Oil yield	0·17	0·05	0·11	0·06
α-Pinene	15·6	4·2	17·0	6·4
Camphene	tr	—	tr	—
β-Pinene	78·8	5·1	75·3	9·1
3-Carene	0·2	0·3	1·0	1·7
Myrcene	3·0	2·0	4·2	5·1
Limonene	0·8	0·5	0·9	0·4
β-Phellandrene	1·6	2·3	1·3	0·7
γ-Terpinene	tr	—	tr	—
Terpinolene	tr	—	tr	—
Methyl chavicol	25·7	19·2	7·4	9·6

* 20 trees were used in either case. Oil yield is expressed in per cent of fresh needle weight, individual terpenoids in per cent of their total, and methyl chavicol in per cent of monoterpenoids as 100%, in conformity with Table 1 of our previous publication.[8]

Representative results obtained are given in Fig. 1 and Table 2. A very strong effect of pollution damage on the per cent of methylchavicol is striking in the case of needles gathered in February and May. Total oil yield was significantly less in injured trees, but the difference could be explained solely on the basis of the reduction in methyl chavicol since total amount of monoterpenoids remained the same. The absence of any differences with needles gathered in July is understandable, as the analysis was performed using juvenile growth, exposed only for a month or so to air pollution, whereas the other needles were exposed for about eight and eleven months, respectively. On the other hand no differences were observed with percentage of individual monoterpenoids.

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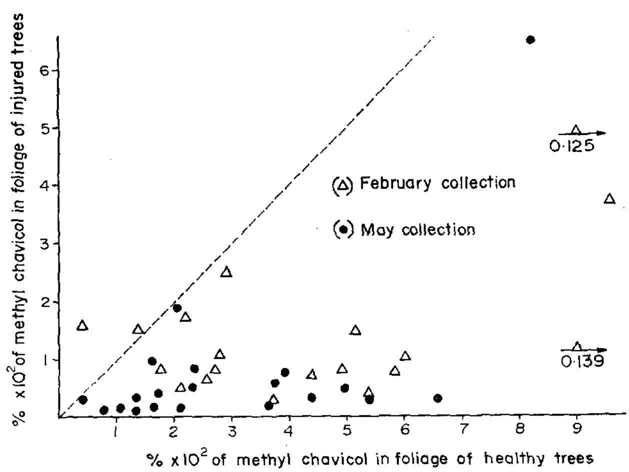

FIG. 1. PLOT OF METHYL CHAVICOL NEEDLE CONTENT FOR THE HEALTHY VS. INJURED TREES. EACH POINT REPRESENTS A SEPARATE TREE PAIR. DASHED LINE INDICATES THE PROBABLE LOCATION OF THE POINTS ASSUMING NO DIFFERENCE BETWEEN TREES PAIRED.

As yet it is impossible to be certain whether the reasons for the differences mentioned are associated with air pollution influencing the biosynthetic paths leading to methyl chavicol, or whether air pollution is preferentially damaging the trees with lower content of methyl chavicol. Of the two alternatives the first seems more attractive, however, and, if substantiated, could indicate disturbances of the reaction paths connected with transformation of sugars to the aromatic compounds, i.e. with the shikimic acid pathways. The effects appear to parallel qualitatively the influence of needle aging on the essential oil composition, reported previously,[8] i.e. the effect of air pollution represents an accelerated sensescence.

TABLE 2. STATISTICAL SIGNIFICANCE OF THE DIFFERENCES BETWEEN HEALTHY AND INJURED PONDEROSA PINES AT 3 DIFFERENT SAMPLING PERIODS. t-VALUES OVER DEGREES OF FREEDOM

Needle age No. of pairs Date sampled	8 months 19 Feb. 1967	1 month 12 July 1967	11 months 20 May 1968
Total oil	− 2·910 (17)*	1·924 (11)	− 5·367 (19)*
Total monoterpenoids	0·051 (18)	1·500 (11)	1·860 (19)
Methyl chavicol	− 4·922 (18)*	1·852 (11)	− 5·670 (19)*
α-Pinene	1·166 (18)	0·315 (11)	0·853 (19)
β-Pinene	1·125 (18)	0·065 (11)	1·626 (19)
3-Carene	1·000 (18)	0·314 (11)	2·000 (19)
Myrcene	1·523 (18)	1·000 (11)	1·520 (19)
β-Phellandrene	1·163 (18)	0·467 (9)	0·657 (18)
Limonene	0·833 (18)	1·702 (11)	1·449 (19)

* Significant on 1 % level. No other differences were significant even at 5 % level. The first three variables were expressed in per cent of the weight of the green foliage, the rest as percentages of their total. Signs refer to decrease in volatile components observed with injured trees.

EXPERIMENTAL

The collections were made in the San Bernardino National Forest near Strawberry Peak from healthy vs. diseased trees paired in terms of age, height, stem diameter, dominance, stand density, exposure, slope, soil type and proximity. In February 1967 and May 1968, 20 pairs of trees were sampled. The sample amounted to 12 pairs in July 1967. With respect to air pollution injury the trees were rated on a scale 0–9.[1] Those trees with 0–1 ratings were considered healthy, while the injured trees included in the study rated from 4 to 7. The collections were made between 9 a.m. and 2 p.m., and the collected needles were stored first in ice chests, and then in a freezer in air-tight 1 qt. jars. In all cases, needles from the terminal (youngest) growth were considered only. The collections were performed in February 1967, July 1967 and May 1968.

The method of needle oil analysis has been described earlier.[8] Data was analysed using a paired *t*-test.

Acknowledgements—We are indebted to the National Science Foundation for Grant No. GB 7363, which supported this work.

Key Word Index—*Pinus ponderosa*; Pinaceae; air pollution; terpenes; methyl chavicol.