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A STUDY OF THE EFFECT OF LIGHT ON THE EMISSION OF TERPENES FROM CERTAIN WOODY PLANTS

by

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A Graduate Student Independent Study Project

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(NASA-CR-148142) A STUDY OF THE EFFECT CF N76-25759 LIGHT ON THE EMISSION OF TERPENES FRCM CERTAIN WOODY PLANTS (OLD DOMINION UNIV., NORFOLK, VA.) 16 P HC \$3.50 CSCL 02F UNCLAS G3/51 28347

MATERIALS AND METHODS

A Varian Aerograph Model 1400 single column gas chromatograph, equipped with a hydrogen flame ionization detector was used in this study. The hydrogen flame detector was utilized in this study because it responds specifically and linearly to the number of carbon atoms in an organic compound.

Air samples were passed through a 6 foot by 0.125 inch 0.D., stainless steel column, packed with 5% carbowax 20M on acid-washed chromosorb W, 60/80 mesh. The thermal regions were maintained at 120°C for the injector, 60°C for the column, and 180°C for the detector. The operating flow rates for nitrogen, hydrogen and air were 15 ml/min., 30 ml/min., and 300 ml/min. respectively. The electrometer of the gas chromatograph was operated at maximum attenuation (IX) and at a sensitivity range of 10^{-11} amps per millivolt (amps/m.v.). A Varian Aerograph Model A-25 10 inch potentiometric strip chart recorder was operated at a setting of 1 mv. and a chart speed of 0.5 inches per minute (in/min.). In conjunction with the strip chart recorder a Varian Aerograph 200 Series disc integrator and a Model 610 automatic printer were used. Some pure terpene compounds, the ones most frequently emitted by woody plants, were used for standardization. The standards used were isoprene, alpha pinene, beta pinene, camphene, myrcene, alpha terpineol and limonene.

The following woody plants were utilized in this study: Atlantic White Cedar (<u>Chamaecyparis thyoides</u>), American Holly (<u>Ilex opaca</u>), Sweet gum (<u>Liquidambar styraciflua</u>), Red Bay (<u>Persea borbonia</u>), Loblolly pine (<u>Pinus</u> <u>taeda</u>), Live oak (Quercus virginiana), Willow oak (<u>Quercus phellos</u>) and Bay berry (<u>Myrica pensylvanica</u>).

Plants 2 or 3 feet in height were collected from various sites in the Great Dismal Swamp, Suffolk, Virginia with the exception of bay berry which

was collected at Duck, North Carolina. The plants were maintained in a greenhouse to allow an acclaimation period of at least two weeks before analysis.

The plants were enclosed in plexiglass ch mbers. Two of the chambers were 1 foot square by 3 feet high, and one was 2 feet high by 3 feet wide by 1 foot deep both were equipped with rubber septum ports for air sampling.

A Hamilton model 1002 gas tight syringe, with a 2 inch 23 gauge needle was used for taking 1 ml. air samples from the chambers. Lodge and Pate (1966), reported that the use of hypodermic needles as critical orifices in air sampling experiments were more than satisfactory.

The plants were placed inside the plexiglass chambers on a table in the laboratory and the chambers were sealed with 2 inch aluminized duct tape. Duplicate sets of samples were collected from each plant in each chamber.

The first sampling set, constituted the control i.e. plants not illuminated, during subsequent sampling sets the plants were illuminated with 150 watt Westinghouse flood lamps, placed 1 foot from the base of the chambers. The light intensity given off by each lamp was approximately 300 lux. In each sampling set 1 ml. air samples were taken from each of the plants in a group at the end of 1, 3, 5, and 7 hours. All of the 1 ml. samples were injected directly into the gas chromatograph immediately after withdrawal from the chambers. After each group of plants were analysed their leaves were dried at 105°C for 48 hours and weighed.

RESULTS AND DISCUSSION

Six distinct terpene components were resolved from the 8 plants analyzed by gas chromatography, but only 5 of these components were definitely identified. The sixth chemical component had a retention time of 0.39 minutes and appeared in the samples taken from the 2 oak species (Table 1). This component is probably one of the lighter hydrocarbon compounds such as butene. The hemiterpene, isoprene, was the only terpene emitted by all the plants in this study (Table 1). Alpha pinene, a monoterpene, was emitted by 4 of the 8 plants in this study. It was also noted that Beta pinene was emitted by all the Alpha pinene producers except Atlantic White Cedar. The shrubs in this study, redbay and bayberry, were the only 2 plants to emit myrcene. The Willow and live Oak, were the only 2 plants to emit exactly the same components, but the components differed quantitatively for the 2 plants (Table 1, 5 and 7).

The quantitative output of terpene components by each plant varied considerably during the illumination-sampling period (Tables 3). However, upon further investigation the terpene output seemed to be related to total leaf surface area per plant and total dry leaf weight per plant. The correlation coefficient between these factors and terpene output was greater than 0.9 (Table 2).

During this study three things were continually observed. One, the temperature inside the plant chambers would gradually rise from 25°C to 30°C during the illumination period. Two, heavy condensation formed on the inside walls of most of the chambers, within an hour or two, after illumination and remained throughout the sampling period. Three, there was considerable variability in the level of detectable terpenes available for sampling among the plants studied.

The increase in temperature within the chambers during the illumination period is attributable to the heat emanating from the flood lamps. However, air temperatures within the chambers never rose above 30°C.

The condensation that formed on the inside walls of the chambers resulted from plants undergoing increased transpiration. This is logical since transpiration is temperature dependent. Following the temperature increase the relative humidity inside the chambers rose to or near 100%, and excess moisture condensed on the relatively cooler chamber walls.

The variability in the level of terpenes emitted by each plant could be attributed to several factors: 1) differences in the total leaf surface and leaf biomass (Table 2), 2) adhesion of vapors to chamber walls, which were laden with condensate, 3) terpene photo disintegrated, and 4) reduction in terpene emissions due to stomatal closure due to excess water loss.

Tables 3-9 present the log of the areas for each component emitted by each of the plants during the illumination period. The data for isoprene, Alpha pinene, camphene, Beta pinene and the unknown showed a steady decrease in the level of detectable terpenes, through the course of study. However, Alpha and Beta pinene components emitted by loblolly pine showed a gradual increase during the last hour of illumination. Myrcene, the component emitted by the 2 shrubs redbay and bayberry was the only component emitted to display a somewhat different behavior (Table 6 and 9).

I ALANT

COMPOSITION OF VAPORS EMITTED FROM THE PLANTS ANALYZED

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			•		Pi	LECK	DINC	F PA	GE BL
167 2:64 MYRCENE				1	×				
164-165 2:50 Beta Pinene				×	×	;	•		
159-160 2:26 CAMPHENE		×						×	×
155-156 2:12 Alpha Pinene		×		×	×		×		
34 1:00 ISOPRENE		×	×	×	×	×	×	×	× .
7 0.39 LNNXNU								×	×
BOILING POINT (°C) RETENTION TIME (min): TERPENE :	TWL	Chamaecyparis thyoids	Ilex optica	Liquidambar styraciflua	Myrica pensylvanica	Persea borbonia	Pinus taeda	Quercus phellos	Quercus virginiana

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LEAF MEASUREMENT AND WEIGHTS FOR THE PLANTS IN THIS STUDY

PLANT	TOTAL NUMBER LEAVES PER PLANT	TOTAL LEAF SURFACE AREA PER PLANT (cm ²)	TOTAL DRY LEAF WEIGHT PER PLANT (gm)
C. thyoides	350	8,750.0	21.70
I. opaca	70	2,005.8	14.92
L. styraciflua	16	2,040.0	4.00
<u>M</u> . pensylvanica	77	3,765.3	7.30
P. borbonia	29	728.6	1.60
r. taeda	360	1,080.0	00°6
Q. phellos	140	7,700.0	14.00
Q. virginiana	. 120	5,382.0	14.95

DAR	*NANOLITERS/ml of SAMPLE	1,200.0 37.9 11.3 1,249.2	800.0 71.8 <u>17.8</u> 889.6	700.0 61.8 <u>14.5</u> 776.3	500.00 34.00 <u>9.68</u> 543.68
COMPOSITION OF VAPORS FROM ATLANTIC WHITE CEDAR	A COMPONENT OF TOTAL AREA	95.87 3.02 <u>1.11</u> 100.00	88.89 8.51 2.60 100.00	90.05 7.71 2.24 100.00	91.93 5.96 2.11 100.00
	*AREA (mm ²)	603 19 629	376 36 4 23	362 31 402	262 17 285
QUANTITATIVE	COMPONENT	I soprene Alpha p inene Camphene TOTAL	Isoprene Alpha pinene Camphene TOTAL	Isoprene Alpha pinene Camphene TOTAL	Isoprene Alpha pinene Camphene TOTAL
	TIME IN HRS.	7	M	v.	~

QUANTITATIVE COMPOSITION OF VAPORS FROM ATLANTIC WHITE CEDAR

TABLE 3

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· AREA WAS COMPUTED BY PEAK HEIGHT METHOD

X DILUTION FACTOR - QUANTITY UNKNOWN NANOLITERS COMPUTED BY: area unknown area standard

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QUANTITATIVE COMPOSITION OF VAPORS FROM AMERICAN HOLLY

NANOLITERS/m1 of SAMPLE	705	632.50	385	312
A COMPONENT OF TOTAL AREA	100	100	100	100
AREA (mm ²)	330	296	180	146
COMPONENT	Isoprene	Isoprene	Isoprene	Isoprene
TIME IN HRS.	T	m	S	٢

NANOLITERS AL OF SAMPLE	 1.100 <u>29.1</u> 1,129.1	1,000 67.8 1,067.8	 600 61.3 661.3	600 6422
· CONPONENT OF TOTAL AREA	12.17 84.87 2.96 100.00	11.41 81.54 7.05 100.00	13.24 77.45 <u>9.31</u> 100.00	6.55 86.04 7.41 100.00
<u>AREA (mm²)</u>	74 516 <u>18</u> 608	68 486 <u>596</u>	54 316 408	23 302 <u>351</u>
COMPONENT	Unknown I soprene Camphene TOTAL	Unknown I soprene Camphene TOTAL	Unknown I sojyr ene Camjyhene TOTAL	Unknown I soprene Camphene TOTAL
TINE IN HRS.	1	m	۰, N	, L

QUANTITATIVE COMPOSITION OF VAPORS FROM LIVE OAK

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QUANTITATIVE COMPOSITION OF VAPORS FROM RED BAY

NANOLITERS/M1 of SAMPLE	310.00 48.25 358.25	275.00 <u>38.50</u> 313.50	270.00 83.50 353.50	183 . 50 64.25 2 47.75
COMPONENT OF TOTAL AREA	90.91 90.00	91.49 <u>8.51</u> 100.00	82.89 <u>17.11</u> 100.00	81.13 18.87 100.00
AREA (mm ²)	150 15 165	129 141	126 152	88 106
COMPONENT	I sopr cne Myrcene TOTAL	I sopre ne Myrcene TOTAL	I sopr ene Myrcene TOTAL	I soprene Myrcene TOTAL
TINE IN ILES.	4	n	دە	۲.

TABLE 6

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REA NANOLITERS/m1 of SAMPLE	 682.50 <u>16.13</u> 698.63	 977.50 <u>58.00</u> 1035.50	 960.00 <u>25.75</u> 985.75	 927.50 <u>38.75</u> 966.25
COMPONENT OF TOTAL AREA	13.16 84.21 2.63 100.00	10.16 83.30 6.53 99.99	$\begin{array}{c} 4.12\\ 92.59\\ \underline{3.29}\\ 100.00\end{array}$	2.75 92.16 <u>5.08</u> 99.99
AREA (mm ²)	50 320 <u>380</u>	56 459 <u>36</u> 551	20 450 486	13 435 472
COMPONENT	Unknown I sopr ene Camplene TOTAL	Unknown I supr ene Campliene TOTAL	Unkinwu I sopreñs Camphene TOTAL	Unknown I sopr ene Camphene TOTAL
TIME IN HRS.	-	m	ທ	۲

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QUANTITATIVE COMPOSITION OF VAPORS FACE WILLOW OAK

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QUANTITATIVE COMPOSITION OF VAPORS FROM LOBLOLLY PINE

NANOLITERS/ml of SAMPLE	180.00	162.50	136,50	119.50	106.50
	311.00	283.00	187,25	32.00	75.75
	234.50	<u>183.25</u>	<u>199,75</u>	21.50	34.75
	725.50	628.75	523,50	173.00	217.00
S COMPONENT OF TOTAL AREA	24.14	24.52	28.07	68.29	48.08
	44.83	45.80	41.23	19.51	36.54
	31.03	29.68	<u>30.70</u>	<u>12.20</u>	<u>15.38</u>
	100.00	100.00	100.00	<u>100.00</u>	100.00
AREA (mm ²)	84 156 <u>348</u>	76 142 <u>92</u> 310	64 94 <u>70</u> 228	56 16 82	50 38 164 104
COMPONENT	Isoprene	Isoprene	Isoprene	Isoprene	Isoprene
	Alpha pinene	Alpha pinene	Alpha pinene	Alpha pinene	Alpha pinene
	Beta pinene	Beta pinene	Beta pinene	Beta pinene	Beta pinene
	TOTAL	TOTAL	TOTAL	TOTAL	TOTAL
TIME IN HRS.	4	m	υ.	٢	o ,

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TIME IN HRS.	COMPONENT	AREA (mm ²)	& COMPONENT OF TOTAL AREA	NANOLITERS/ml of SAMPLE
r .	Isoprene Alpha pinene Bcta pinene Myrcene TCTAL	174 74 - 5 284	61.26 26.06 1.76 10.92 100.00	370.00 147.50 10.85 99.50 627.85
÷	Isoprene Alpha pinene Beta pinene Myrcene TVTAL	162 68 9 282	57.45 24.11 3.19 <u>15.25</u> 100.00	135,50 19,53 138,83 638,86
ئى	Isoprene Alpha pinene Beta pinene Myrcene TOTAL	158 28 6 276	57.25 10.15 2.17 <u>30.43</u> 100.00	337.50 55.75 13.00 269.75 676.00
۲	Isoprene Alpha pinene Beta pinene Myrcene TOTAL	134 16 4 191	70.16 8.38 2.09 <u>19.37</u> 100.00	285.00 32.00 8.68 <u>118.75</u> <u>944.43</u>
σ	Isoprene Alpha pinene Jeta pinene Myrcene TOTAL	102 14 3 187	54.55 7.49 1.60 <u>36.36</u> 100.00	217.50 28.00 6.50 217.50

QUANTITATIVE COMPOSITION OF VAPORS FROM BAY BERRY

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LITERATURE CITED

- Hendrickson, J.B., Cram, J.D., Hammond, G.G. 1970. Organic Chemistry, 3rd ed., McGraw-Hill Book Co., N.Y.
- Jaffe, L.S. 1967. Effects of Photochemical Air Pollution on Vegetation with Relation to the Air Quality Requirements. J. Air Poll. Cont. Ass., <u>17</u>, 38.
- Lodge, J.P., Pate, J.B. 1966. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Poll. Cont. Ass., <u>16</u>, 197.
- Rasmussen, R.A. 1972. What Do the Hydrocarbons from Trees Contribute to Air Pollution? J. Air Poll. Cont. Ass., 22, 537.
- Rasmussen, R.A., Holden, M.W. 1972. Analyses of C₅ and C₁₀ Hydrocarbons in Rural Atmospheres. J. Air Poll. Cont. Ass., <u>72</u>, 3.
- Rasmussen, R.A., Went, F.W. 1965. Volatile Organic Material of Plant Origin in the Atmosphere. Proc. Nat. Acad. Sci., <u>53</u>, 215.
- Von Rudloff, E., Socd, V.K. 1969. Gas Liquid Chromatography of Terpenes XVIII. Can. J. Chem., <u>47</u>, 2081.
- Went, F.W. 1965. Organic Matter in the Atmosphere and its Possible Relation to Petroleum Formation. Proc. Nat. Acad. Sci., <u>53</u>, **215**.