

Revisiting the effects of paraquat treatment on different *Pinus*

Jaime Fernandes¹, Andreia Soares¹ e Miguel Pestana¹*

Abstract. Paraquat is a chemical compound that stimulates the exudation of pine resin. Treatment with this compound also induced lightwood in some pine trees. Lightwood formation in these species could potentially increase the quantity and quality of naval stores chemicals from these species.

Key words: oleoresin, tall oil, turpentine, *Pinus sylvestris*, *P. strobus*, *P. flexilis*, *P. mariana*, *P. glauca*.

Lembrando o efeito do tratamento com paraquat em diferentes *Pinus*

Sumário. O Paraquat é um composto químico que estimula a exsudação de resina de pinheiro. O tratamento com este composto induziu também a formação de mais resina no tronco em alguns pinheiros. A formação da resina no tronco nestas espécies pode potenciar o aumento da quantidade e da qualidade dos produtos químicos para sector de resina natural proveniente destas espécies.

Palavras-chave: Oleoresina, Tall oil, Aguarrás, *Pinus sylvestris*, *P. strobus*, *P. flexilis*, *P. mariana*, *P. glauca*.

¹ Instituto Nacional de Investigação Agrária e Veterinária, I.P., Quinta do Marquês, 2780-157 Oeiras, Portugal.

* Corresponding author: miguel.pestana@iniav.pt

Introduction

The upstream bottleneck of the resin value chain lies in the stages between resin extraction—namely exudation and breakage during collection from the tree – and the often careless transportation of resin from the pine forest to the processing plant, both of which critically affect the entire downstream process. The product obtained from this first stage of this chain can be improve, as a resin richer in volatiles and cleaner will be received at the factory, increasing yield and reducing operating costs.

This change is imposed downstream of this Value Chain, as the naval store chemicals market is attractive and extremely demanding, with fierce competition. Quality products differentiated from petroleum industry products, with competitive prices, are essential.

Resin is naturally produced and stored in dedicated resin canals or resiniferous channels, distinct from sap. These channels serve a defence function against insects and other harmful agents, creating a protective layer on the trunk that contributes to tissue healing and eliminates fungi and insects (DUARTE, 2016).

In resin tapping, incisions are made in the tree trunk that stimulate the formation of new resin canals and, consequently, increased resin production. This resin is collected in a container attached to the tree (a bag or jug).

Resin production is seasonal, occurring 6-9 months a year during the dry season. During this period, each tree is visited individually, approximately every 15 days, to open a new wound and apply the stimulating paste.

The following are notable weaknesses upstream of this Sector:

I. Low resin production per tree (~1.5 kg per harvest), losses of 20 to 40% associated with the collection container, and a lack of genetic improvement initiatives for resin production.

II. A sharp decrease in the area suitable for resin extraction in pine forests and a tendency toward an increase in young age groups that are still too small for resin extraction.

III. Lack of labour and low productivity among resin tappers, which increases labour costs (they account for one-third of the total cost of resin at the factory gate).

IV. Some lack of interest among forest owners in resin extraction and investment in pine forests, resulting from misinformation (e.g., economic viability

of pine forests, resin extraction and wood quality, resin extraction and plant health, resin extraction in risk management).

V. Payment for resin and its derivatives at lower reference prices for petroleum derivatives

So, we have the opportunity to increase the activity's profitability by applying existing know-how (extraction techniques and genetic improvement) and also to address the weaknesses associated with competition from resin from other sources (notably Brazil) (with a factory gate cost 20-40% lower than that of domestic resin). Based on these premises, we recall the available information on the importance of Paraquat as stimulating paste in pine resiling. (KOMISSAROV *et al*, 1968, ROBERTS, 1973, ROBERTS *et al.*, 1973)

The paraquat-induced lightwood in *Pinus sylvestris* (RANUA, 1975), *P. pinaster* (DAVID *et al*, 1975) and *P. radiata* (SIOUMIS and LAU, 1976) has been investigated, but we will show the potentially increased of the quantity and quality of naval stores derived from other species. David R. Roberts and Willian J. Peters treated sets of pines with paraquat placed into increment boreholes or ax frills (Table 1).

Table 1 - Pines treated with paraquat (CONNER *et al.*, 1977)

Species	Date	
	Treated ^a	Harvested
Eastern White pine (<i>Pinus strobus</i> L.)	22-6-73	26-5-76
Scotch pine (<i>Pinus sylvestris</i> L.)	22-6-73	18-11-75
Scotch pine (<i>Pinus sylvestris</i> L.) ^b	19-10-73	18-11-75
Black spruce (<i>Pinus mariana</i> (Mill.) B.S.P.)	21-6-73	25-5-76
White spruce (<i>Pinus glauca</i> (Moench) Voss)	21-6-73	26-5-76
Limber pine (<i>Pinus flexilis</i> James)	19-6-73	15-9-75

^a Treated with 5 ml of ¼%, 1% or 5% aqueous paraquat placed in a 10 cm³ ax frill. The solutions contained 0.1% of a wetting agent.

^b Treated as described in footnote "a" except solutions were placed into an increment borehole.

It has been shown that a zone of dead, necrotic phloem (inner bark) extended upward from the paraquat-treatment site in all the treated trees. The cambium associated with this dead zone was also killed (no new growth occurred behind the dead phloem after treatment. The wood immediately behind the dead phloem was desiccated. Usually, the zone of dead phloem was associated with external

resin exudation that extended up a tree. The height to which the dead zone extended increased as paraquat concentration increased. The dead phloem and the associated desiccated wood decreased in area as it extended upward and followed any spiral grain in the tree. Blue stain fungi were usually observed within the desiccated wood, but was limited to the lower portions of a tree. (CONNER *et al.*, 1977)

Although increases in tall oil (non-volatile there extractives) and in turpentine were observed in almost all the treated species, true lightwood induction occurred in only the treated *Pinus* spp. In the species that did not lighter, traumatic resin ducts were often observed at the edges of the desiccated wood extending into the adjacent wood formed after paraquat treatment.

The tall oil and the turpentine contents of all of the treated ones had been determined.

Materials and Methods

Species treated with paraquat, treatment methods, and data trees were treated and harvested are given in Table 1.

The trunks were cut into 1.5 m sections starting 0.5 m below the treatment site. The sections starting at the bottom were labelled A, B, C, etc. One section above any visible effect of the paraquat treatment was always studied. Pairs of adjacent 3 cm thick disk were cut at 30 cm intervals for each section. Each pair consisted of a "research" disk used for chemical analysis.

The research disks were immediately frozen and used for determining non-volatile ether extractives (used as a measure of tall oil precursors) and turpentine. Wedges of lightwood and wood for use as controls were excised from each of the research disk.

This frozen wood was chopped into 1 cm by 10 cm sticks, ground in a Wiley mill to pass an 8 mm mesh screen. For turpentine analysis a portion of this coarse sawdust was mixed with 1 % aqueous sodium hydroxide and the turpentine collected by steam distillation. Tall oil (non-volatile ether extractives) was determined by extracting a portion of the sawdust with diethyl ether in a Soxhlet apparatus for 8 hours. The ether was evaporated and the residue dried at 100°C in vacuo (15 mm Hg) and weighed. The percentages of tall oil, turpentine and moisture were them calculated based on tall oil (and turpentine) free oven-dried weight.

Turpentine from this samples were analysed by gas chromatography on 5% Carbowax 20M using diethylcarbitol as an internal standard.

Results and discussion

The characterization of paraquat-treated jack pine, eastern white pine, black spruce and white spruce based on CONNER *et al.* (1977) data, are given in Table 2 through 6.

Summarized in Table 7 and 8 are the quantitative GLC analyses of turpentine from the lightwood and the control wood of the treated pines.

The control wood from paraquat-treated pines contained lower quantities of tall oil and turpentine compared to maximal contents of tall oil and turpentine observed in the lightwood. The tall oil and the turpentine contents of the control wood were usually slightly elevated compared to those of wood from untreated trees.

Scotch, red and jack pine treated with paraquat responded with the greatest increase in tall oil and turpentine.

Table 2 - Tall oil, turpentine and moisture content for paraquat treated Scotch pine^a

Section	Tall oil		Turpentine		Moisture		<i>n</i>	
	LW	CW	LW	CW	LW	CW	LW	CW
A	25.5±7.0 ^b	5.5±1.1 ^a	10.8±3.3 ^b	0.7±0.3 ^a	67.3±15.2 ^a	128.5±9.0 ^a	12	13
B	10.7±6.4 ^a	5.0±1.1 ^a	3.5±2.9 ^a	0.6±0.3 ^a	91.5±43.0 ^a	134.5±10.7 ^a	12	13
C	8.9±5.6 ^a	4.8±1.8 ^a	2.7±2.6 ^a	0.5±0.3 ^a	102.8±46.7 ^a	138.8±14.5 ^a	12	13
D	14.6±10.0 ^{ab}	25.5±7.3 ^a	5.3±4.3 ^{ab}	0.5±0.1 ^a	83.0±53.5 ^a	141.0±9.9 ^a	6	6
E	17.1±9.4 ^{ab}	25.5±7.4 ^a	6.1±4.1 ^{ab}	0.5±0.2 ^a	83.0±50.6 ^a	144.8±18.2 ^a	4	4
F	10.0±9.3 ^{ab}	25.5±7.5 ^a	3.0±4.2 ^a	0.4±0.1 ^a	122.0±48.0 ^a	146.3±21.5 ^a	3	3
Mean	14.5	4.8	5.2	0.5	91.6	139		

Note: ^a Contents are reported as percentages (%) based on tall oil and turpentine free oven-dried wood weight. CW - control wood, LW - lightwood.

^b Sections are 0.5m long; Section A begins 0.5m below site of paraquat treatment.

ANOVA $p < 0.05$. Different letters, in the same column, express significant differences between each type of fruit for each parameter.

Table 3 - Tall oil, turpentine and moisture content for paraquat treated Eastern white pine^a

Section	Tall oil		Turpentine		Moisture		<i>n</i>	
	LW	CW	LW	CW	LW	CW	LW	CW
A	11.5±2.9	7.1±1.9	2.1±0.7	0.5±0.2	96.2±15.1	153.7±18.8	6	6
B	10.9±7.6	5.5±1.3	1.7±1.5	0.4±0.1	102.0±33.6	166.3±14.2	6	6
C	7.4±3.0	4.9±1.0	0.8±0.6	0.3±0.1	114.3±33.7	145.8±30.0	6	6
D	8.2±3.0	5.1±1.1	1.2±0.5	0.4±0.1	74.3±7.1	154.0±9.5	3	3
E	7.0±2.0	4.8±1.0	0.9±0.7	0.3±0.1	104.3±62.8	148.3±15.6	3	3
F	8.8±1.6	4.3±1.6	1.8±0.4	0.3±0.1	74.5±2.1	151.0±12.7	2	2
G	8.3±3.0	4.1±1.5	1.7±0.6	0.3±0.1	54.0±9.9	143.5±0.7	2	2
H	6.3±1.3	4.3±2.3	1.2±0.5	0.3±0.1	84.0±73.5	139.0±12.7	2	2
I	5.0±0.0	4.5±0.0	0.3±0.0	0.2±0	139.0±0.0	154.0±0.0	1	1
Mean	8.2	5	1.3	0.3	93.6	150.6		

Note: ^a Contents are reported as percentages (%) based on tall oil and turpentine free oven-dried wood weight. No significant difference, $p < 0.05$, for the values in each column

Table 4 - Tall oil, turpentine and moisture content for paraquat treated limber pine^a

Section	Tall oil		Turpentine		Moisture		<i>n</i>	
	LW	CW	LW	CW	LW	CW	LW	CW
A	8.2±3.7 ^b	5.8±1.5 ^a	1.0±0.9 ^a	0.4±0.1 ^a	67.3±20.1 ^a	81.0±7.5 ^a	11	7
B	5.9±1.8 ^{ab}	5.1±1.6 ^a	0.5±0.3 ^a	0.4±0.2 ^a	70.8±19.3 ^a	83.1±6.9 ^a	11	7
C	4.6±1.7 ^a	4.1±0.8 ^a	0.5±0.4 ^a	0.3±0.3 ^a	70.9±14.3 ^a	78.9±6.9 ^a	11	7
D	4.8±1.8 ^a	4.1±1.4 ^a	0.4±0.3 ^a	0.2±0.1 ^a	65.6±17.9 ^a	73.8±6.4 ^a	8	4
Mean	5.9	4.8	0.6	0.3	68.7	79.2		

Note: ^a Contents are reported as percentages (%) based on tall oil and turpentine free oven-dried wood weight. CW - control wood, LW - lightwood. ANOVA $p < 0.05$. Different letters, in the same column, express significant differences between each type of fruit for each parameter.

Table 5 - Tall oil, turpentine and moisture content for paraquat treated Black spruce^a

Section	Tall oil		Turpentine		Moisture		<i>n</i>	
	LW	CW	LW	CW	LW	CW	LW	CW
A	3.9±0.9	1.4±0.4	1.2±0.5	0.2±0.1	33.8±4.5	83.4±8.2	6	8
B	3.1±1.0	1.2±0.3	1.0±0.5	0.1±0.0	38.7±9.5	83.6±9.1	6	8
C	2.3±0.9	1.2±0.4	0.7±0.6	0.2±0.1	48.3±21.8	85.3±6.7	6	8
D	2.3±1.3	1.4±0.4	0.7±0.7	0.1±0.1	25.0±6.6	94.0±6.1	3	3
E	2.1±1.6	1.5±0.4	1.0±0.9	0.2±0.1	35.0±4.6	95.0±11.4	3	3
F	1.5±0.4	1.4±0.2	0.3±0.2	0.2±0.0	67.0±39.6	100.0±14.1	2	2
Mean	2.5	1.4	0.8	0.2	41.3	90.2		

Note: ^a Contents are reported as percentages (%) based on tall oil and turpentine free oven-dried wood weight. CW - control wood, LW - lightwood. No significant difference, $p < 0.05$, for the values in each column

Table 6 - Tall oil, turpentine and moisture content for paraquat treated White spruce^a

Section	Tall oil		Turpentine		Moisture		<i>n</i>	
	LW	CW	LW	CW	LW	CW	LW	CW
A	6.7±2.7	2.1±0.6	2.1±1.2	0.2±0.1	36.2±4.3	132.0±23.5	6	8
B	4.6±1.4	2.0±0.7	1.3±0.7	0.2±0.2	40.0±11.7	131.3±28.8	6	8
C	4.3±2.3	1.9±0.6	1.2±1.3	0.2±0.1	91.5±67.3	122.9±57.5	6	8
D	6.0±1.3	3.0±0.8	2.2±1.0	0.3±0.1	69.0±28.3	134.0±60.8	2	2
E	6.2±5.0	2.6±0.6	2.0±2.3	0.2±0.1	90.5±87.0	141.0±35.4	2	2
Mean	5.6	2.3	0.8	0.2	41.3	90.2		

Note: ^a Contents are reported as percentages (%) based on tall oil and turpentine free oven-dried wood weight. CW - control wood, LW - lightwood. No significant difference, $p < 0.05$, for the values in each column

Table 7 - Turpentine composition of paraquat-treated pines

Component	Turpentine composition ^a					
	Scotch ^b		Eastern white		Limber	
	CW	LW	CW	LW	CW	LW
α -Pinene	18-81	20-85	35-60	43-59	3-11	6-16
Camphene	t-3	t-1	1-2	1-2	t	t
β -Pinene	t-56	1-59	7-24	16-27	1-4	2-8
Sabinene	0-1	0-2	0-1	t-4	t-4	1-6
3-Carene	0-58	0-57	t	t	t-29	t-31
Myrcene	1-3	1-3	t	t	1-2	1-2
Limonene	t-3	t-3	1-2	1-2	5-19	10-28
β -Phellandrene	0-4	0-5	t	t	t	t
Other ^c	4-23	2-14	18-52	16-37	64-76	39--71

Note: ^a t- trace, CW - control wood, LW - lightwood.

^b Control wood data are from control wood areas of all trees studied; lightwood data, from trees treated with only 5% paraquat.

^c Mostly high boiling components not eluted under GLC conditions used for analysis.

Table 8 - Turpentine composition for paraquat-treated conifers exclusive of pines

Component	Turpentine composition ^a			
	Black Spruce ^b		White Spruce	
	CW	LW	CW	LW
α -Pinene	22-38	14-36	9-31	12-27
Camphene	t-1	t-1	t-3	t-3
β -Pinene	12-29	8-44	11-35	20-44
3-Carene	t-19	t-23	1-9	2-19
Myrcene	t-2	1-2	t-1	1-2
Limonene	2-14	5-20	t-3	t-2
β -Phellandrene	1-3	1-4	1-4	1-6
Other ^c	23-60	10-43	35-70	15-46

Note: ^a t- trace, CW - control wood, LW - lightwood.

^b Control wood data are from control wood areas of all trees studied; lightwood data, from trees treated with only 5% paraquat.

^c Mostly high boiling components not eluted under GLC conditions used for analysis.

Paraquat treatment of the spruces produced an intermediate response. Thus, the control wood contained concentration 1 to 2% tall oil and 0.1 to 0.3 % turpentine compared to maximal contents of concentration 5 to 9 % tall oil and 2 to 4 % turpentine observed in the lightwood areas. Thus, lightwood induction in spruce trees might be of limited commercial significance.

The lightwood turpentine contained less light-boiling constituents than did the control wood turpentine from the same species. Some compositional changes were observed between the turpentine from the lightwood and that from the control wood, but these differences were not dramatic.

Conclusions

The height of lightwood induction upward in a tree increased as concentration of paraquat increased.

No dramatic compositional changes were observed for turpentine from lightwood vs. that from control wood of these species, i.e., the chemical composition of turpentine from conifers is altered by the application of paraquat and it increases the levels of α -pinene, β -pinene and limonene in almost all conifers studied.

References

- CONNER, A.H., Diehl, M. A., Wroblewska, H, Rowe, J.W., 1977. Effects of paraquat treatment of Northern and Western conifers, *Lightwood Research Coordinating Council Proceedings - Annual Meeting*, January 18-19, Atlantic Beach, Florida, USA, pp 34-56.
- DAVID, R., Bentejac, R., Raoux, H., Blicq, W., Launay, J., 1975. Increase in oleoresin content in the wood maritime pine (*Pinus pinaster* Sol.) trunks treated with diquat or paraquat, *C.R. Hebd. Seances Academy Sciences*, D287, pp 1841-1845.
- DUARTE, C. A, 2016. *Evolução do sector da resinagem em Portugal*. Dissertação de Mestrado em Recursos Florestais. Coimbra.
- KOMISSAROV, D.A., Frolov, Yu. A., Egorova, E.A., 1968. Effects of chemicals on resin yields during tapping, *Cidrolis. Lesokhim. Prom.*, 21, p. 21.

- RANUA, J., 1975, Increasing pitch content of pine by herbicide treatment Paperi *Ja Puu*, 57, pp. 597-599.
- ROBERTS, D. R., 1973. Inducing lightedwood in pine trees by paraquat treatment, *U.S. Department of Agriculture Forestry Service Southeastern Forest Experimental Station Ashville, N.C. Research Note SE-191*, 4p.
- ROBERTS, D.R., Joye, N.M. Jr., Proveaux, A. T., Peters, W. I., Lawrence, R. V., 1973. A new and more efficient method of naval stores production, *Naval Stores Review*, pp. 4 - 5.
- SIOUMIS, A. A., LAU, L. S., 1976. Paraquat-induced resinosis in *Pinus radiata*. Pt. I. The effect of paraquat on *Pinus radiata*, *Appita*, 29, pp. 272-275.