ISSN 1070-3632, Russian Journal of Bioorganic Chemistry, 2023, Vol. 49, No. 7, pp. 1654–1662. © Pleiades Publishing, Ltd., 2023.

Seasonal Changes in the Composition of Scots Pine (*Pinus sylvestris* L.) Oleoresin, Measured by the NMR Method

E. D. Skakovskii[a,*], L.Yu. Tychinskaya[a], E. I. Gapan'kova[a], I. A. Latyshevich[a], E. H. Popoff[b], and S. A. Lamotkin[c]

[a] *Institute of Physical and Organic Chemistry, National Academy of Sciences of Belarus, Minsk, 220072 Belarus* [b] *Central Botanical Garden, National Academy of Sciences of Belarus, Minsk, 220072 Belarus*
[c] *Belarusian State Technological University, Minsk, 220006 Belarus*
**e-mail: sed@ifoch.bas-net.by*

Received June 1, 2021; revised September 30, 2021; accepted December 9, 2021

Abstract—Seasonal changes in the composition of Scots pine oleoresin were analyzed by ^{1}H and ^{13}C NMR spectroscopy. Due to favorable weather conditions (positive temperatures on the sampling dates throughout the year) samples for each of the 12 months were obtained and studied. Chloroform ($CDCl_3$) solutions of oleoresin were investigated. Eight resin acids: abietic, dehydroabietic, isopimaric, levopimaric, neoabietic, palustric, pimaric, and sandaracopimaric acids, as well as six monoterpenes: camphene, limonene, myrcene, α-pinene, β-pinene, and terpinolene, were identified and quantified. It was revealed that the amounts of the oleoresin released and its constituent α-pinene decreased at low temperatures. Other monoterpenes were not detected within the measurement accuracy in this period of time. It was supposed that monoterpenes, formed in smaller amounts during the period of pests' anabiosis, play the key role in the control of coniferous insect pests. The contents of dehydroabietic, isopimaric, neoabietic, pimaric, and sandaracopimaric acids were found to vary insignificantly throughout the year. An interrelation between the amounts of abietic, levopimaric, and palustric acids in the oleoresin composition was revealed. The observed interrelation was supposedly associated with low-temperature catalytic reactions of levopimaric acid isomerization leading to predominant formation of abietic acid. It was suggested that these processes should be taken into account to avoid errors in determining the contents of these acids in the oleoresin even in the case of statistical analysis.

Keywords: *Pinus sylvestris* L., oleoresin, monoterpenes, resins acids, NMR spectrum

DOI: 10.1134/S1068162023070816

INTRODUCTION

Forests covering 39.8 percent of the territory of Belarus rank among its most important natural resources. Scots pine (*P. sylvestris* L.) with up to 40 m height and up to 1.2 m diameter of the base has a dominant position among the forest cultures growing in Belarus. Resinous and durable, pine tree wood is used in residential and technical construction, in interior joinery and carpentry. The oleoresin present in the resin ducts of pine under pressure of 120–200 kPa is secreted when its bark and wood are mechanically wounded, e.g., by tapping. Pine oleoresin finds application in medicine and provides a valuable raw material for the chemical industry; it contains ≤25% by volume essential oil (turpentine), which is removed by steam distillation, leaving behind solid phase known as rosin. Turpentine is used for manufacture of varnishes, solvents, fragrant chemicals, adhesives, and other items. Rosin is useful in making soap, paper, rubber, and varnishes and paints.

Review [1] described in detail the chemical reactions involving oleoresin components, monoterpenes (MT) and resin acids (RA). MT and RA are present in different pine tree tissues simultaneously. The contents of these components in the needles of *P. sylvestris* were analyzed by gas chromatography-mass spectrometry (GC/MS) [2].

The cones' extractives of *Pinus halepensis*, *P. brutia*, *P. pinea*, *P. sylvestris*, and *P. nigra* were analyzed by GC/MS [3]. The same method was applied to nonvolatile compounds research of needles, trimmed saplings, and outer bark of *P. densiflora* [4] and *P. thunbergii* [5]. The resin of lodgepole pine (*P. contorta*) studied by GC [6].

Acidic and neutral diterpenes of the oleoresin of *Pinus nigra* were analyzed by ^{13}C NMR spectroscopy in $CDCl_3$ [7, 8]. ^{1}H and ^{13}C NMR spectral assignments of abietane diterpenes from *Pinus heldreichii* and *Pinus nigra subsp. nigra* was made in different solvents: $CDCl_3$, C_6D_6, CD_3OD, and $(CD_3)_2CO$ [9].

Quantitative determination of the RA from maritime pine (*P. pinaster*) oleoresin was carried out using ^{13}C NMR in $CDCl_3$ [10]. Abietane diterpenes were prepared and studied by NMR spectroscopy, and assignments for the ^{1}H and ^{13}C NMR peaks were obtained by means of correlation spectroscopy [11].

Using ^{1}H and ^{13}C NMR spectroscopy, we studied the composition of the Scots pine resin balsams [12], the gum resin proper [13, 14], and the gum rosin derived therefrom [14].

We applied GLC and NMR measurements to evaluate the impact of industrial pollution, as well as of radioactive and toxic elements on the chemical composition of the Scots pine resin [15, 16].

Investigation of the stimulatory effect produced by various adjuvants to commercial oleoresin-inducing paste on the resin yield from slash pine *Pinus elliottii* Engelm. var. *elliottii* revealed its seasonal variation [17]. The highest yield of oleoresin was observed from the tapped trees during summer. Thus, the pine oleoresin composition has been studied in detail, but its seasonal changes have not been sufficiently analyzed [18]. At the same time, the changes in the content of terpenes emitted from the pine needles throughout the year were monitored by the NMR and GLC, and the contents' dynamics of pinenes, carene, camphene, limonene, bornyl acetate, caryophyllene, and cadinene was analyzed [19]. The essential oil composition of pine needles differs from oleoresin's (turpentine) that one, it was thus of interest to study the seasonal variation of the composition in relation to pine oleoresin.

Seasonal and geographical variation of terpenes, resin acids, and total phenolics in the nursery grown seedlings of Scots pine (*Pinus sylvestris* L.) were described in [20]. It was found that, in spring, there was more of 3-carene, α-pinene, β-pinene, (+)-sabinene, and total mono-terpenes in the pine shoots, and less myrcene and tricyclene compared to autumn. In autumn, the concentrations of levopimaric and dehydroabietic acids were higher, while those of palustric, abietic, and neoabietic acids were lower.

The composition and physicochemical properties of the oleoresin of Scots pine trees growing in Poland were studied in [21]. Specifically, 343 oleoresin samples, taken monthly from May to September in 1976–1979 at tapping sites in 5 forest districts, were analyzed. The content of turpentine in the collected oleoresin samples was found to decrease from 19.7% in May to 16.5% in September. The main turpentine component was α-pinene, whose content was estimated at 55.6 and 49.7% for the southern and northern regions, respectively. The RA content in the rosin increased from 92.0% in May to 93.2% in September, irrespective of the oleoresin collection site.

Literature search revealed very scanty information on the month-over-month changes in the pine oleoresin components. At the same time, analysis of this kind of data is of interest for clarifying the biochemical synthesis routes in Scots pine and for identifying the time when its composition is dominated by compounds of consumer significance.

In view of the above-said, the goal of this study was to investigate seasonal changes in the composition of the Scots pine oleoresin harvested throughout the year from the same tree (to avoid statistical smoothing of the quantitative data, which could level off the differences). The investigation was carried out using high-resolution NMR spectroscopy, ensuring achievement of the goal set.

EXPERIMENTAL

Oleoresin samples were collected from a 40-year-old Scots pine tree growing in the Nothern forest park

Table 1. Weather conditions on the oleoresin sampling dates

Date	Temperature, °C	Note
August 12, 2019	+25	cloudy, rainy
September 12, 2019	+24	partly cloudy
October 12, 2019	+15	mainly cloudy
November 12, 2019	+6	partly cloudy
December 12, 2019	+1	rainy
January 12, 2020	+2	mainly cloudy
February 12, 2020	+2	mainly cloudy
March 12, 2020	+6	clear
April 12, 2020	+8	partly cloudy
May 12, 2020	+7	rainy
June 12, 2020	+27	clear
July 12, 2020	+13	cloudy, rainy
August 12, 2020	+18	clear

of Minsk. Samples were taken on the 12th day of every month, from August 2019 to August 2020 inclusive. For oleoresin extraction, a ~4 cm^2 section of bark was removed from the tree stem. Before sampling, the selected area was cleaned, and the oleoresin released within 24 h was collected. Depending on the season, the sampled amount varied from 0.01 g in winter to 0.50 g in summer. Table 1 summarizes the weather conditions for the pine oleoresin sampling dates.

Thus, throughout the year, on the sampling dates, the temperature was positive, which favored oleoresin release from the pine tree. A maximum value (+27°C) was observed in June, and a minimum value (+1°C), in December. For NMR analysis, solutions of the oleoresin in $CDCl_3$ were prepared by dissolving ~10 mg of the sample in winter and ~80 mg in summer, in 0.5 mL of the solvent.

NMR spectra were recorded on an AVANCE-500 spectrometer operated at 500 and 125 MHz frequency for ^1H and ^{13}C nuclei, respectively, at a temperature of 20°C. The quantitative proton spectra were recorded with 30° pulses, and the carbon spectra, with 60° pulses, separated by 5 s relaxation delays in both cases. For identification of compounds, the ^1H and ^{13}C spectra of the supposed RA and MT were preliminarily recorded under identical conditions. With stoichiometric ratio between the integrated intensities of the ^1H NMR signals from individual compounds the conditions for quantitative NMR spectroscopy were met. The number of scans, depending on the concentration, was 128 or 512 for ^1H NMR spectra and ~1000 or 15000 for proton-decoupled ^{13}C NMR spectra. The spectra were acquired using 64K data points and zero-filled to 128K data points, with 0 and 1 Hz line broadening applied for the ^1H and ^{13}C NMR spectra, respectively, and Lorentzian line shape being assumed. Phase and baseline corrections were done manually prior to integration. Recording ^{13}C NMR spectra was essential for a more complete identification of the oleoresin components.

For the compounds (in the mixture) ^1H NMR spectra chemical shifts were determined using the $CDCl_3$ solvent impurity signal, $CHCl_3$ (δ = 7.27 ppm), and those in the ^{13}C NMR spectra, using the signal of the solvent proper (δ = 77.7 ppm). All the experimental data were obtained and processed with the use of the XWIN-NMR 3.5 software package.

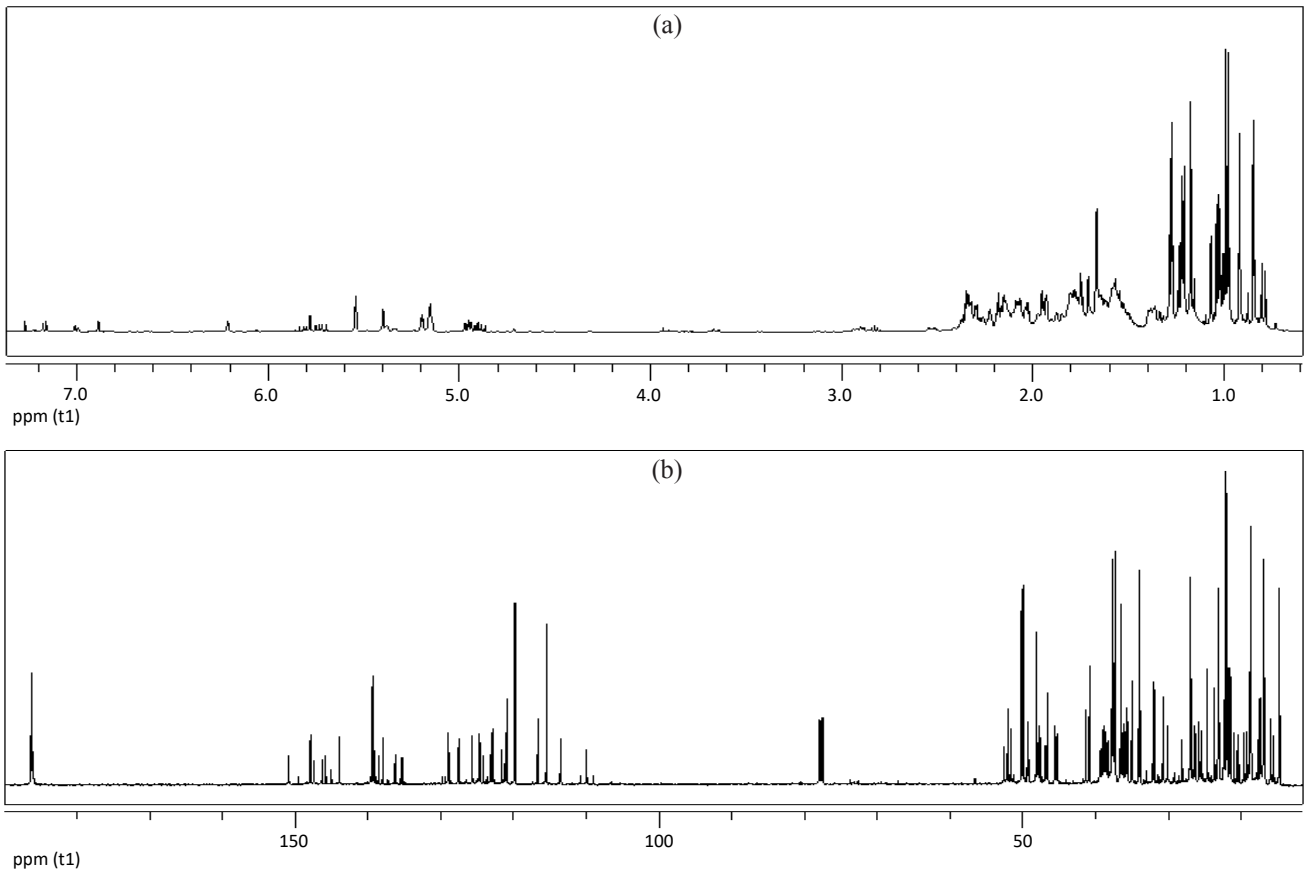

Fig. 1. NMR spectra of the solution of the pine oleoresin (September) in $CDCl_3$: (a) ^1H and (b) ^{13}C.

Quantitative calculations were based on the integrated intensities of the groups of signals that correspond to the compounds moieties in the proton spectra.

RESULTS AND DISCUSSION

Figure 1 shows the NMR spectra of the solutions of the oleoresin samples collected in September (IX) 2019. Eight RA were detected, namely, abietic (1), dehydroabietic (2), isopimaric (3), levopimaric (4), neoabietic (5), palustric (6), pimaric (7), and sandaracopimaric (8) acids, as well as five MT, namely, camphene (9), limonene (10), α-pinene (12), β-pinene (13), and terpinolene (14). Also, myrcene (11) was present in some of the samples.

The assignment of the signals in the NMR spectra of the oleoresin was given in [12, 13, 22–24]. Almost all the identified compounds, except for terpinolene, exhibit individual non-overlapping signals in the region of double bonds and aromatics, as presented in Fig. 2 with signal numbers provided. This enabled quantitative calculations using the integrated line intensities, to which purpose the individual signal of terpinolene, observed in the spectrum at $\delta = 2.77$ ppm, was used. Analysis of the spectra showed that, in the sample collected in September, the main resin acids were levopimaric (24.7%), palustric (12.5%), and pimaric (10.6%) acids; sandaracopimaric acid was the least abundant (1.1%). Among monoterpenes, α-pinene dominated (15.1%), with the rest accounting for less than 1%.

Figure 3 shows the NMR spectra of the oleoresin sample collected in February (II) 2020. In this case, seven resin acids were detected: abietic (1), dehydroabietic (2), isopimaric (3), neoabietic (5), palustric (6), pimaric (7), and sandaracopimaric (8). By contrast to sample (IX), abietic was the main (57.8%), with pimaric (10.4%)

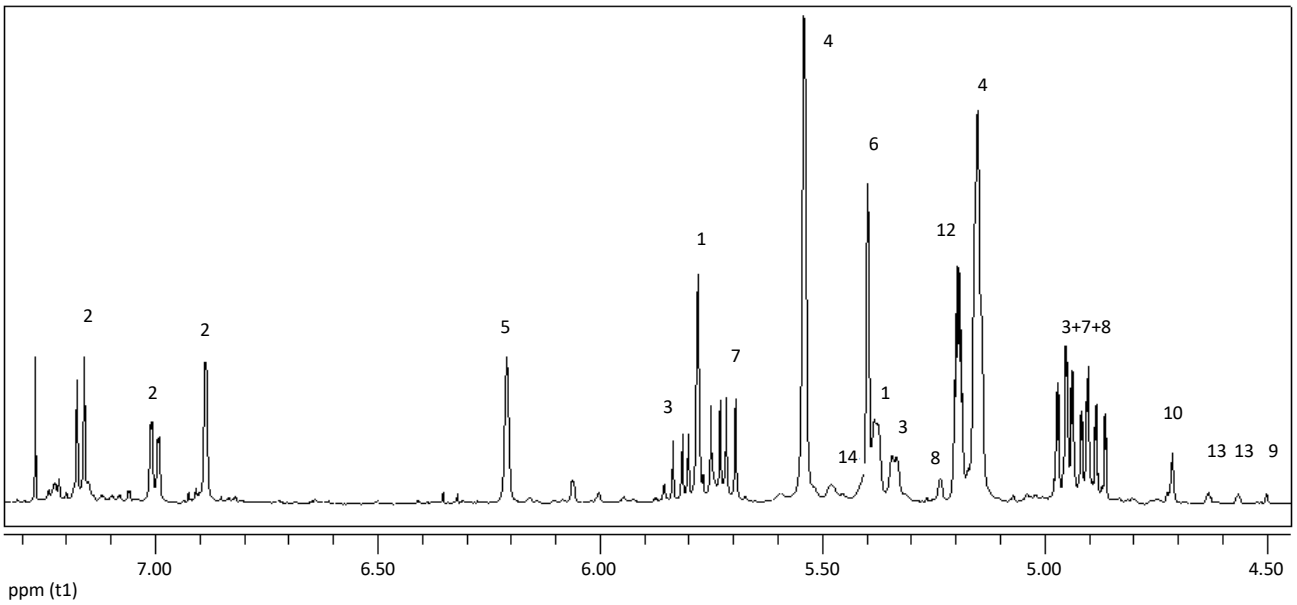

Fig. 2. ^{1}H NMR spectrum of the solution of the pine oleoresin (September) in $CDCl_3$, region of double bonds and aromatics.

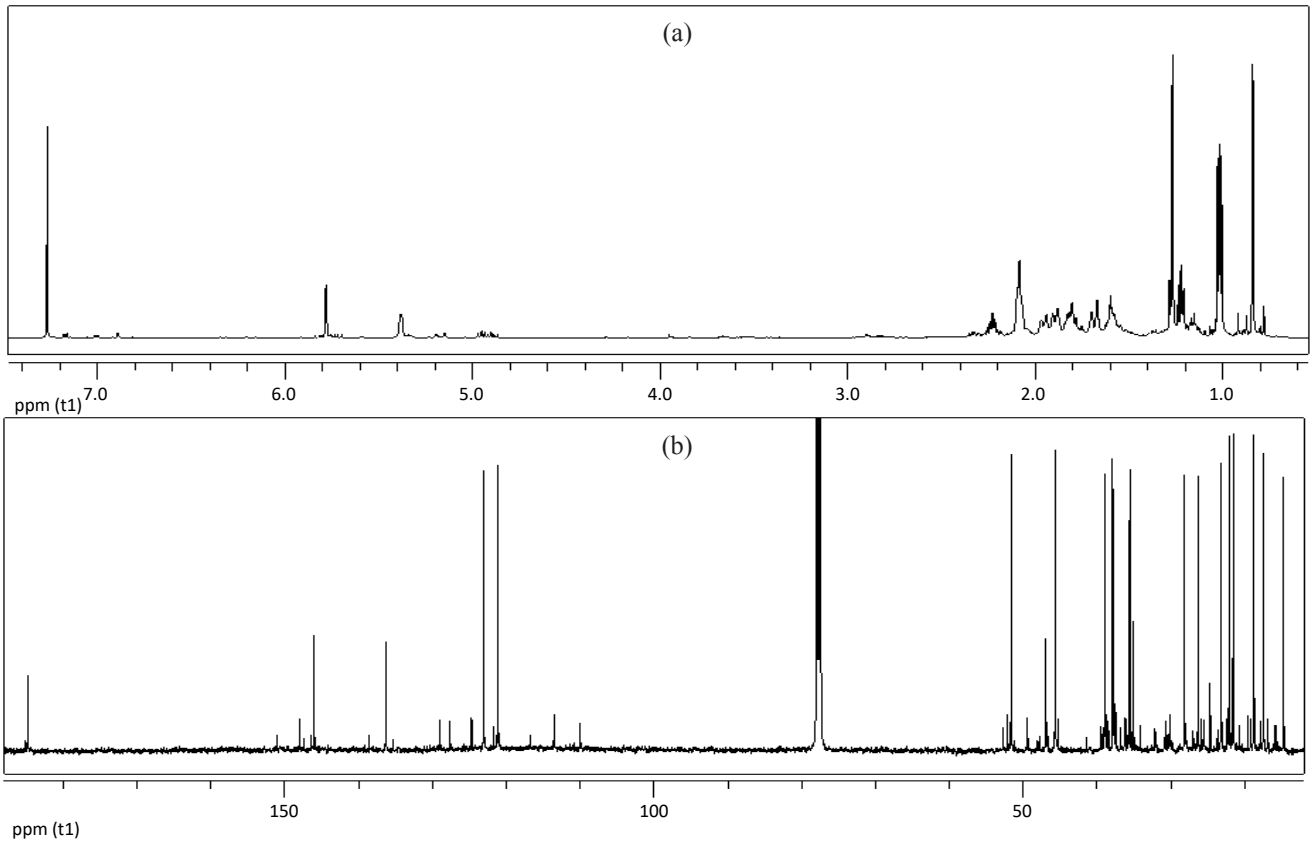

Fig. 3. NMR spectra of the solution of the pine oleoresin (February) in $CDCl_3$: (a) ^{1}H and (b) ^{13}C.

Table 2. Changes in the composition of the Scots pine oleoresin throughout the year (mol %)

Resin acids/ Monoterpenes	2019					2020								
	VIII	IX	X	XI	XII	I	II	III	IV	V	VI	VII	VII*	VIII
Abietic	21.0	8.1	26.6	5.0	48.2	39.7	57.8	49.7	18.2	20.2	8.7	8.9	27.4	17.8
Dehydroabietic	3.1	6.6	4.2	2.8	9.5	5.8	5.9	4.8	11.6	3.4	3.2	2.4	2.9	2.7
Isopimaric	5.0	5.5	6.5	4.6	7.7	6.8	7.5	6.9	8.2	4.1	4.8	4.9	4.4	3.9
Levopimaric	–	24.7	–	21.9	–	–	–	–	4.8	–	20.7	14.3	–	–
Neoabietic	9.7	7.6	10.5	6.6	1.0	9.0	1.7	8.6	8.1	9.2	8.4	7.1	6.6	8.2
Palustric	22.4	12.5	24.6	10.9	1.1	11.7	2.2	7.2	21.9	21.9	13.8	14.4	11.4	21.2
Pimaric	7.6	10.6	9.9	7.2	10.0	10.3	10.4	9.5	13.6	6.3	7.9	6.8	6.5	5.9
Sandaracopimaric	1.4	1.1	1.7	0.7	1.5	2.3	1.5	1.8	2.4	1.6	1.3	0.9	1.7	2.6
Camphene	0.4	0.2	0.3	0.4	1.3	–	–	–	–	0.3	0.3	0.3	0.3	0.3
Limonene	1.9	0.8	0.8	2.4	0.3	–	–	–	–	2.3	2.6	3.0	3.0	2.7
Myrcene	0.3	–	–	0.4	–	–	–	–	–	0.5	1.3	0.9	1.1	0.5
α-Pinene	19.2	15.1	8.5	30.9	11.5	8.5	7.0	6.5	4.2	23.4	21.0	28.4	29.1	26.6
β-Pinene	0.7	0.3	0.6	1.1	–	–	–	–	–	0.7	0.8	0.9	0.6	0.8
Terpinolene	1.0	0.8	–	–	–	–	–	–	–	–	–	0.8	0.6	0.7

* Sample VII was diluted 10-fold for recording the spectrum.

being the second most abundant acid. Levopimaric acid was not detected within the measurement accuracy. Among monoterpenes, only α-pinene was revealed, whose content (7.0%) was approximately half that detected in the sample collected in September.

The data on the seasonal changes in the composition of the oleoresin (Table 2) show that, in the period from January to April, the only monoterpene observed was α-pinene, whose content decreased from 8.5 to 4.2% over this period. The α-pinene proportion in the oleoresin was fairly high (reaching 30.9%) in all other months, except for October 2019 (8.5%).

The second most abundant monoterpene was limonene, whose proportion in the oleoresin reached 3.0% in the summer months. Camphene was present in almost the same amount of 0.3% in all the months, except for the period from January to April. Myrcene was not detected during seven months, and in the remaining months its average content was 0.7%. Terpinolene was detected only in four out of thirteen samples, with an average content of 0.8%.

Thus, during the cold period, there was a decrease not only in the total amount of the released oleoresin but also in the content of MT in its composition. In this regard, it is believed that conifers have evolved oleoresin terpenes as a material essential for defense against pests and pathogens and for wound sealing [25]. Monoterpenes, for the most part liquids under the experimental conditions, at near-zero temperatures are more easily released from wood than resin acids. The observed effect apparently suggests the predominance of MT over RA in the protection against woodworms. Probably, in winter, when insects fall into anabiosis, MT are not so important, and their synthesis slows down.

The identified resin acids bear different types of skeletons. Specifically, pimaric, isopimaric, and sandaracopimaric acids have pimarane and isopimarane skeletons, and abietic, levopimaric, neoabietic, and palustric

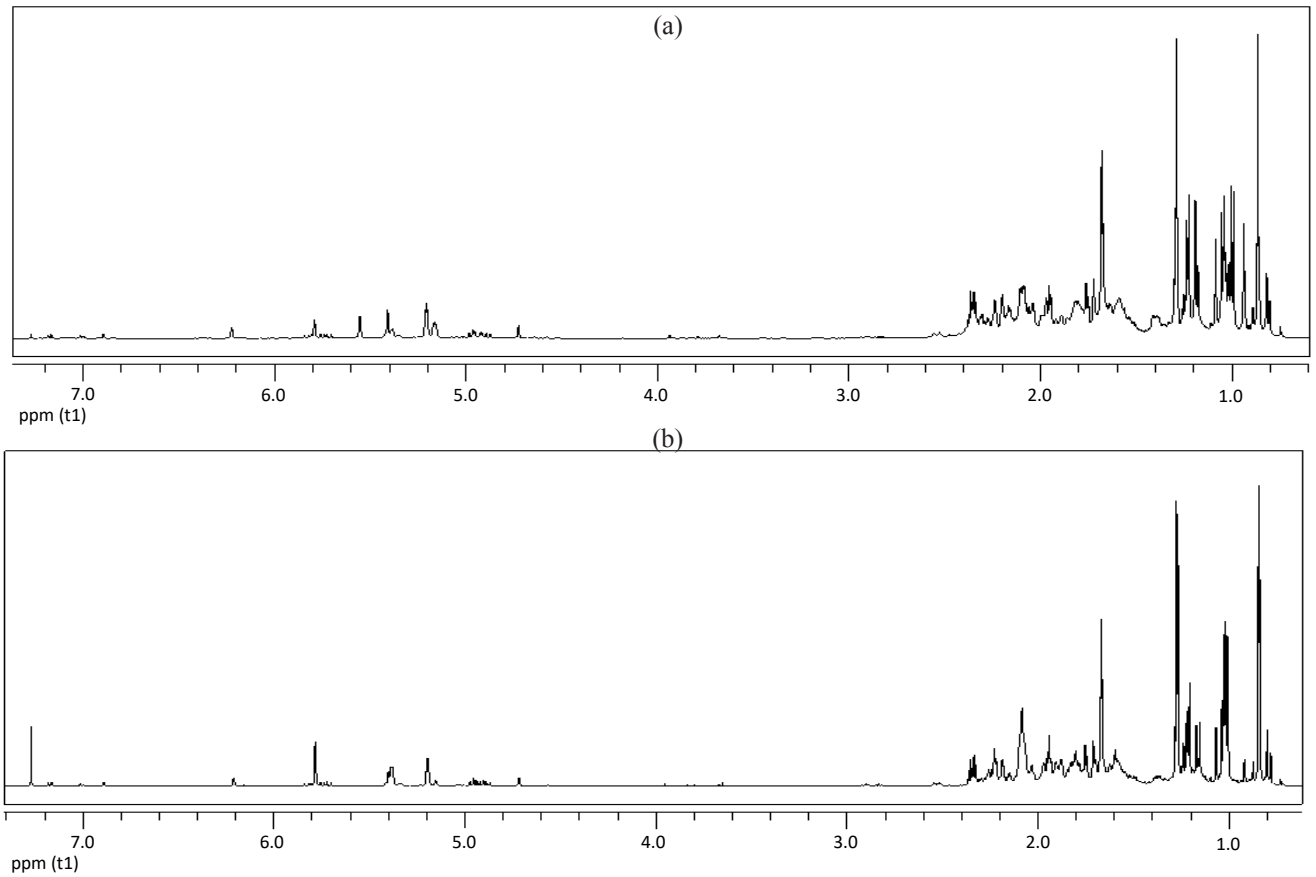

Fig. 4. ^{1}H NMR spectra of (a) concentrated and (b) diluted solution of the pine oleoresin (July) in $CDCl_3$.

acids, abietane skeleton. Also, the oleoresin contains dehydroabietic acid, which aromatic resin acid is associated with the latter type of skeleton [1].

Table 2 shows that the contents of the resin acids with pimarane and isopimarane skeletons changed negligibly throughout the year. The pattern observed for dehydroabietic acid reveals no seasonal changes. The content of neoabietic acid having abietane skeleton also changed negligibly (6.6–10.5%) throughout the study period, except for December and February (1.0–1.7%).

Abietic and levopimaric acids exhibit complex patterns, with their contents being obviously interrelated. Specifically, the absence of levopimaric acid, or its presence in a small amount, suggests an increase in the content of abietic acid in the oleoresin. For example, in winter, the proportion of abietic acid in the oleoresin was ~1/2, while levopimaric acid was completely absent. Seasonal changes in the palustric acid content are difficult to explain.

For the oleoresin sample collected in July 2020, when the component composition of the oleoresin was the fullest, the ^{1}H and ^{13}C NMR spectra were recorded for a concentrated and a 10-fold diluted (^{1}H) solutions (see Table 2 and Fig. 4).

From Table 2 and Fig. 4 it follows that the quantitative composition of the diluted solution of the oleoresin sample collected in July is distinguished by the lack of levopimaric acid and by a nearly tripled content of abietic acid. Such changes can be reasonably explained by the fact that, upon dilution at room temperature, levopimaric acid apparently undergoes low-temperature catalytic isomerization reactions.

Consequently, changes in the content of abietane-type RA appear not only with the season, but are also caused by the different temperature conditions in the course of catalytic reactions. Therefore, to obtain reliable results on the RA synthesis in Scots pine it is necessary either to change the NMR spectra recording conditions in a way such that the effect of the catalytic reactions on the contents of the oleoresin components be avoided or to take these reactions into account in some way.

CONCLUSIONS

Seasonal changes in the Scots pine oleoresin composition were studied by the ^{1}H, ^{13}C NMR spectroscopy. It was found that, in winter, the amounts of the oleoresin released and its constituent monoterpenes decrease, and the proportion of abietic acid, increases. An interrelation was revealed between the contents of abietic, levopimaric, and palustric acids in the oleoresin. It was shown that the observed interrelation is due to the proceeding of fast, probably catalytic, reactions. This suggests that, when determining the content of these acids, even in the case of statistical analysis, one may obtain overestimated contents of abietic and palustric acids and, accordingly, underestimated content of levopimaric acid.

FUNDING

This work was supported by regular institutional funding, and no additional grants were obtained.

ETHICS APPROVAL AND CONSENT TO PARTICIPATES

The authors alone responsible for the content of the paper. This article doesn't have tests involving humans or animals.

Informed consent was not required for this article.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

AUTHOR CONTRIBUTION

E.D. Skakovski, L.Yu. Tychynskaya and E.H. Popoff analyzed the literature data on the topic and implemented spectral studies; A.I. Hapan'kova, I.A. Latyshevich - sampling. All authors participated in discussions and the manuscript preparation.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1. El-Sayed Abdel-Raouf, M. and Abdul-Raheim, M., *BAOJ Chem.*, 2018, vol. 4, no. 1, pp. 1–16.
2. Semiz, G., Heijari, J., Isik, K., and Holopainen, J.K., *Biochem. Syst. Ecol.*, 2007, vol. 35, no. 10, pp. 652–661. https://doi.org/10.1016/j.bse.2007.05.013
3. Kiliç, A., Hafizoğlu, H., Dönmez, I.E., Tümen, I., Sivrikaya, H., Reunanen, M., and Hemming, J., *Eur. J. Wood. Prod.*, 2011, vol. 69, pp. 37–40. https://doi.org/10.1007/s00107-010-0421-2
4. Khokhrina, E.A., Shpatov, A.V., Popov, S.A., Sal'nikova, O.I., Shmidt, E.N., and Um, B.H., *Chem. Natl. Compd.*, 2013, vol. 49, no. 3, pp. 561–565. https://doi.org/10.1007/s10600-013-0673-2
5. Shpatov, A.V., Popov, S.A., Salnikova, O.I., Khokhrina, E.A., Shmidt, E.N., and Um, B.H., *Natl. Prod. Commun.*, 2013, vol. 8, no. 12, pp. 175–1762. https://doi.org/10.1177/1934578X1300801227
6. Lewinsohn, E., Savage, T.J., Gijzen, M., and Croteau, R., *Phytochem. Anal.*, 1993, vol. 4, pp. 220–225. https://doi.org/10.1002/pca.2800040506
7. Rezzi, S., Bighelli, A., Castova, V., and Casanova, J., *Appl. Spectrosc.*, 2002, vol. 56, no. 3, pp. 312–317.
8. Rezzi, S., Bighelli, A., Castova, V., and Casanova, J., *Ind. Crops Prod.*, 2005, vol. 21, pp. 772–778. https://doi.org/10.1016/j.indcrop.2003.12.008
9. Koutsaviti, A., Ioannou, E., Couladis, M., Tzakou, O., and Roussis, V., *Magn. Reson. Chem.*, 2017, vol. 55, pp. 772–778. https://doi.org/10.1002/mrc.4585
10. Ottavioli, J., Paoli, M., Casanova, J., Tomi, F., and Bighelli, A., *Chem. Biodivers.*, 2019, vol. 16, Article ID: e1800482. https://doi.org/10.1002/cbdv.201800482
11. Lee, H.-J., Ravn, M.M., and Coates, R.M., *Tetrahedron*, 2001, vol. 57, no. 29, pp. 6155–6167. https://doi.org/10.1016/S0040-4020(01)00605-6

12. Skakovskii, E.D., Tychinskaya, L.Yu., Gaidukevich, O.A., Kozlov, N.G., Klyuev, A.Yu., Lamotkin, S.A., Shpak, S.I., and Rykov, S.V., *Zh. Prikl. Spektrosk.*, 2008, vol. 75, no. 3, pp. 411–415.
13. Skakovskii, E.D., Tychinskaya, L.Yu., Gaidukevich, O.A., Klyuev, A.Yu., Lamotkin, S.A., Shpak, S.I., and Rykov, S.V., *Coll. of Papers, XV All-Russ. Conf. "Structure and Dynamics of Molecular Systems,"* Yal'chik, 2008, vol. 3, pp. 172–175.
14. Skakovskii, E.D., Tychinskaya, L.Yu., Klyuev, A.Yu., Latyshevich, I.A., Gapan'kova, E.I., and Kozlov, N.G., *Polim. Mater. Tekhnol.*, 2018, Vol. 4, no. 3, pp. 84–88.
15. Shpak, S.I., Lamotkin, S.A., Lamotkin, A.I., and Skakovskii, E.D., *Coll. of Papers, XV All-Russ. Conf. "Structure and Dynamics of Molecular Systems,"* Yal'chik, 2006, vol. 2, pp. 445–458.
16. Shpak, S.I., Lamotkin, S.A., Lamotkin, A.I., and Skakovskii, E.D., *Tr. Belarus. Gos.Tekh. Univ. Ser. 4: Khim, Tekhnol. Org. Veshch.*, 2006, vol. 14, pp. 165–169.
17. Rodrigues-Corrêa, K.C.S. and Fett-Neto, A.G., *Theor. Exp. Plant Physiol.*, 2013, vol. 25, no. 1, pp. 56–61. https://doi.org/10.1590/S2197-00252013000100007
18. Azarov, V.I., Burov, A.V., and Obolenskaya, A.V., *Chemistry of Wood and Synthetic Polymers: Textbook for Higher Educational Institutions*, St. Petersburg: Sankt.-Peterb. Lesotekh. Akad., 1999.
19. Lamotkin, S.A., Skakovskii, E.D., Mekhanikova, E.G., Gil', E.V., and Romanyuk, L.I., *Tr. Belarus. Gos.Tekh. Univ. Ser. 2: Khim. Tekhnol., Biotekhnol., Geoekol.*, 2019, no. 1 (217), pp. 17–24.
20. Nerg, A., Kainulainen, P., Vuorinen, M., Hanso, M., Holopainen, J.K., and Kurkela, T., *New Phytol.*, 1994, vol. 128, no. 4, pp. 703–713. https://doi.org/10.1111/j.1469-8137.1994.tb04034.x
21. Sadlovcka, J., *Pr. Inst. Badlesn.*, 1987, vols. 662–665, pp. 53–71.
22. Skakovskii, E.D., Tychinskaya, L.Yu., Gaidukevich, O.A., Klyuev, A.Yu., Kozlov, N.G., Baranovskii, A.V., and Rykov, S.V., *Coll. of Papers, XV All-Russ. Conf. "Structure and Dynamics of Molecular Systems,"* Yal'chik, 2007, vol. 1, pp. 545–548.
23. Muto, N., Tomokuni, T., Haramoto, M., Tatemoto, H., Nakanishi, T., Inatomi, Y., Murata, H., and Inada, A., *Biosci. Biotechnol. Biochem.*, 2008, vol. 72, no. 2, pp. 477–484. https://doi.org/10.1271/bbb.70570
24. Skakovskii, E.D., Lamotkin, S.A., Tychinskaya, L.Yu., Molchanova, O.A., Matveichuk, S.V., and Sorokina, Yu.M., *Tr. Belarus. Gos. Tekh. Univ. Ser. 4: Khim. Tekhnol. Org. Veshch.*, 2014, no. 4, pp. 211–215.
25. Celedon, J.M. and Bohlmann, J., *New Phytol.*, 2019, vol. 224, no. 4, pp. 1444–1463. https://doi.org/10.1111/nph.15984