ESSENTIAL OIL OF BUDS OF Betula pendula OF YAKUTIA

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UDC 547.913:582.632

The quantitative amounts of the essential oil of the European white birch of the Yakut population in the annual cycle and its component composition have been investigated.

Birch buds have long been used in folk medicine. Preparations obtained from them are being used successfully for treatment of many diseases, and also in perfumery [1, 2].

An important biologically active component of the buds is the essential oil.

In the present paper we consider the results of an investigation of the amounts of essential oil in the buds of Betula pendula Roth. (European white birch) growing in Central Yakutia, the dynamics of its accumulation in the annual cycle, and its component composition.

The steam-distilled essential oil of white European birch buds of the Yakut population consisted of a colorless oily liquid with a pleasant odor. The specific gravity of the product isolated was 0.9694 g/cm^3, and its refractive index n_D^{20} 1.5008. The indices obtained agree with those given in the literature [3].

The amounts of essential oil in the buds depend to a considerable degree on the time of year, which is explained by the occurrence in the plant of various metabolic processes confined to definite times. The dynamics of its accumulation are shown in Fig. 1.

A maximum amount of essential oil (7.1% of the absolutely dry weight) was found in birch buds gathered at the end of September. Then its amount gradually decreased, reaching a minimum in April (3.1%), less than half its autumn level. In May, a spring maximum was observed on the curve of the accumulation of oil but this was 1.5 times smaller than its autumn value.

The amount of essential oil in the buds of the European white birch of Yakutia exceeds the amount found for birch groves of the European part of the country – 5.3% [1] – and for the Krasnoyarsk forest-steppe region – 5.8%. This is apparently due to the low winter temperatures and to the occurrence of spring frost in this region, which has a substantial effect on the vital activity of plants [4]. The observed increase in the yield of oil corresponds to a general law of the change in its amount in plants on their migration from south to north [5].

The separation of the essential oil on a column of silica gel showed that its main components were α-betulenol acetate (21.9%) and caryophyllene (23.2%). There were also considerable amounts of humulene (5.8%), caryophyllene oxide (6.5%), and α- and β-betulenols (4.7 and 6.5%, respectively). The compounds isolated were identified from their IR and PMR spectra and their optical rotations.

In its composition, the oil investigated was similar to the essential oil from buds of the common birch [6]. The presence of betulenols has also been detected in the essential oils of the buds of other birch species [7, 8]. Apparently, the formation of compounds of the caryophyllene series, to which these compounds belong, is dominating in the biosynthesis of sesquiterpenoids in the genus Betula L. We found a sesquiterpene of a different biogenetic group (α-copaene) only in trace amounts. In addition, about 2.5% of paraffins was found in the oil investigated.

The remainder of the oil consisted of a complex mixture of hydrocarbons (4%), alcohols (8%), and polyfunctional compounds (8%) practically inseparable on the usual sorbents and

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0009-3130/87/2306-0666$12.50

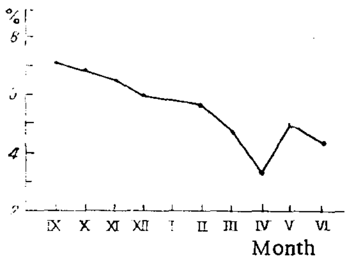

Fig. 1. Change in the amounts of essential oil in birch buds during the annual cycle.

sorbed irreversibly on impregnated sorbents. GLC results confirmed the interpretation made. The chromatogram exhibited about 40 peaks, seven of which were the main ones. Six of these components were identified. The nature of a number of monoterpene oxygen-containing and sesquiterpene compounds was established from their relative times: α- and β-pinenes, camphene, β-myrcene, Δ^3-carene, β-phellandrene, bornyl acetate, and bisabolene. Together they made up 7-12% of the total amount of components.

EXPERIMENTAL

Trial areas (25) were located in birch groves with different types of herbage on the territory of the Yakutsk station of the Forest and Timber Institute of the Siberian Branch of the USSR Academy of Sciences at a distance of 30 km to the north of Yakutsk [9]. Branches were cut from the north sides of the central parts of 50-70 trees per month. The buds (200-250 g) were plucked from them in the course of 1-2 days after they had been cut.

The essential oil was isolated by steam distillation in duplicate. Its yield was determined volumetrically with allowance for the solubility of the oil in the water layer of the separator, and the physicochemical indices were determined by traditional methods.

The composition of the essential oil was studied by column and gas-liquid chromatography. In the first case, chromatography was performed on a column of air-dry silica gel with petroleum ether having gradientwise additions of diethyl ether. The components of the oil were separated by GLC in packed (with DNP and SE-30 as stationary phases) and capillary glass (PMS, 31 m) columns on Tsvet-100 and Chrom-41 chromatographs. The IR spectra of the components isolated were analyzed on a UR-20 instrument, the ^{1}H NMR spectra on a Varian HA-56/60 spectrometer, and angles of optical rotation on Zeiss polarimeters.

SUMMARY

1. The annual cycle of accumulation of the essential oil in the buds of the European white birch of the Yakutsk population has been investigated. Its maximum is observed in September and its minimum in April.

2. The main components of the essential oil have been identified. High amounts of α-betulenol acetate and of caryophyllene have been found in it.

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FREQUENCIES AND INTEGRAL INTENSITIES OF THE LACTONE AND ESTER CARBONYLS OF NATURAL GUAIANOLIDES

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UDC 547.944/945

The frequencies and integral intensities of the IR bands of the stretching vibrations of lactone and acyclic ester carbonyls at C-8 of ten natural guaianolides and their derivatives, and of three model compounds have been studied. The most probable interpretation of the change in the value of $A\nu_{C=O}$ and $\nu_{C=O}$ of the lactone carbonyl have been suggested. In elegin and some of its derivatives, acroptilin, chlorohyssopifolin B, and eleganin, a lowering of the values of $A\nu_{C=O}$ and $\nu_{C=O}$ in comparison with dihydroelegin, hexahydroelegin, and the hydroxylactone of cynaropicrin is caused by nonvalent interactions of the lactone carbonyl with the α-exocyclic double bond. The increase in $A\nu_{C=O}$ and $\nu_{C=O}$ in dihydroelegin, hexahydroelegen, and the hydroxylactone of cynaropicrin is due to the angular strain of the γ-lactone ring. It has been shown that in an acyclic side chain at C-8 an increase in the integral intensity and in the frequency of the α,β-unsaturated ester carbonyl relative to guaianolides in which the terminal vinyl group at C-17 is absent is due to a conjugation effect.

It is known that the frequencies of the absorption bands in IR spectra due to the stretching vibrations $\nu_{C=O}$ in lactones are characteristic, and there are, therefore, grounds for assuming that the integral intensities of these bands can serve as a criterion for evaluating electronic and stereochemical changes taking place in the lactone molecules. In contrast to coumarins, chromones, and xanthones [1], there is no analysis in the literature of the frequencies and, in particular, the integral intensities of $\nu_{C=O}$ of sesquiterpene lactones [2]. We have studied the frequencies and integral intensities of the IR bands in the 1600-1800 cm^{-1} region, which correspond to the stretching vibrations of a carbonyl group in a γ-lactone ring and of an ester carbonyl group in an acyclic side chain at C-8 of the guaianolide series.

Table 1 gives the frequencies and integral intensities of the absorption bands of the carbonyl groups in guaianolides (IV-XIII) investigated. Analysis of the figures in the Table leads to the following results. The integral intensity (A) of the IR band of the carbonyl group of the lactone ring of each of compounds (IV)-(X) with an exocyclic double bond at C-11 amounts to 4.60-5.00 practical units (10^4 liter·mole^{-1}·cm^{-2}), and the absorption frequency corresponding to it is 1765 ± 5 cm^{-1}.

In the case of an alkyl substituent in the α-position of the γ-lactone ring, as, for example, in hydrodroelegin (XI) and hexahydroelegin (XII), the value of $A\nu_{C=O}$ rises to 5.60-6.00 pr.u., and the value of $\nu_{C=O}$ shifts in the high frequency direction by 8-10 cm^{-1}.

On comparing the model compounds (I-III) it may be noted that the presence of α-exocyclic double bond in the cyclopentanone ring (compound (II)) considerably decreases the integral intensity ($A\nu_{C=O}$ = 1.75 pr.u.) and the frequency ($\nu_{C=O}$ = 1727 cm^{-1}) of the carbonyl group in comparison with cyclopentanone ($A\nu_{C=O}$ = 3.0 pr.u., $\nu_{C=O}$ = 1748 cm^{-1}).

Institute of the Chemistry of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 805-811, November-December, 1987. Original article submitted April 3, 1987.