TERPENOIDS OF THE NEEDLES OF Picea abies

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The composition of the terpenoids of the neutral petroleum-ether-soluble substances from an isopropanol extract of the needles of the Norway spruce has been studied. The main components of the extractive substances are polyprenol acetates, alcohols with the labdane type of structure, and epimanool and epitorulosol. It has been shown that the terpenoids from the needles differ in composition from the extractive substances of the trunk part of the tree and those from the oleoresins of the spruces Picea abies, P. ajanensis, and P. obovata.

The woody verdure of Picea abies (L.) (Karst) (Norway spruce) is used for chemical processing. With the aid of a technology using gasoline as extractant, a provitamin concentrate, sodium chlorophyllin, needle wax, an essential oil, and a balsamic paste are obtained from it.

The composition of the extractive substances, particularly the terpenes of the needles, which form the main element of the woody verdure (the proportion of needles in technical woody verdure is 50-70%) has been studied inadequately. Information is given in the literature on the compositions of the essential oils [1-3], the mineral components and the acids [1], and also some vitamins [4].

The extractive substances (5.2% on the weight of the absolutely dry needles) isolated with petroleum ether from an isopropanol extract (38.6%) were separated in the usual way [5] into acids (21.9% on the petroleum-ether-soluble substances) and neutral substances (75.9%). From the neutral substances a series of fractions were isolated by column chromatography which differed with respect to the polarity of their components. Information on the separation is given in Table 1.

The main classes in the fraction of neutral nonpolar extractive substances from Norway spruce needles were esters and alcohols. The proportion of substances eluted from the columns by diethyl ether and ethanol was high. They contained considerable amounts of green pigments and waxy substances. The fractions from the second to the seventh eluted from a column of silica gel had colorations ranging from orange to yellow, probably because of the presence of carotenoids, while from the seventh fraction onwards they were green.

The first and second fractions consisted of hydrocarbons. The terpenes, after separation from the alkanes (2.2% on the neutral substances) consisted of mono-, sesqui-, and diterpenes. Their composition was established by the GLC method: α-pinene (31.8% on the fraction of mono- and sesquiterpenes), camphene (26.9%), β-pinene (7.0%), 3-carene (2.5%), myrcene (0.4%), and limonene (1.2%) were the main monoterpene components; cyclosativene (0.3%), α-ylangene and copaene (0.8%), longicyclene (0.5%), longifolene (2.9%), caryophyllene (2.7%), γ-muurolene (0.8%), α-muurolene (2.1%), α-humulene (3.8%), δ- and γ-cadinenes (13.0%), and calamenene (2.2%) were the main sesquiterpene components. β-Phellandrene and γ-terpinene were identified in very small amounts. The composition of the diterpenes of European spruce needles included the set of tricyclic compounds of the pimaric and abietic types that are common for conifers. Isopimaradiene (30.5%) and dehydroabietadiene (35.4%) were the main components. In addition to these, abietadiene (13.3%) and pimaradiene (12.5% on the diterpenes) were identified.

The composition of the monoterpenes of the Norway spruce needles is close to that of the monoterpenes from the needles of other species of Picea [1-3] in which the ratio of α-pinene and camphene is nearly 1:1 and differs from the composition of the monoterpenes of

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TABLE 1. Results of the Separation of the Neutral Substances by Column Chromatography

Fraction No.	Eluent	Amount		Remarks
		g	%	
1	Petroleum ether	1,11	5,2	Hydrocarbons
2	Petroleum ether-ether (98.2)	0,22	1,0	Hydrocarbons
3	" " (95:5)	9,80	45,6	Esters, aldehydes, oxides. IR spectrum: 1720-1740 cm^{-1}
4	" " (92:8)	0,77	3,6	Esters and alcohols. IR spectrum: 1720-1730 and 3615 cm^{-1}
5	" from (85:15) to (70:30)	1,70	7,9	Alcohols. IR spectrum: 3620 with inflection at 3640 cm^{-1}
6	" from (70:30) to (1:1)	1,87	8,7	Alcohols. IR spectrum: 3630 cm^{-1}
7	" from (1:1) to (30:70)	0,90	4,2	Sterols. IR spectrum: 3620 cm^{-1}. The R_f value of the fraction was equal to that of sitosterol (TLC)
8	" from (30:70) to (15:85)	1,87	8,7	
9	Diethyl ether	1,56	7,3	Chlorophyll derivatives and waxy substances
10	Ethanol	1,67	7,8	
	Total	21,47	100,0	
	Taken from separation	21,74		
	Losses	0,27	1,3	

the trunk part of the tree, the bark, and the oleoresin [6-9]. The sesquiterpenes of Norway spruce needles are close in composition to those of the oleoresin of the Yeddo spruce [10] and of the Siberian spruce [11] but differ by a higher content of cadenenes from the composition of the sesquiterpenes of the oleoresin and essential oils of the genus Pinus [11-15].

On a silica gel column, fraction 2 yielded the main component of the triterpene hydrocarbons – squalene (PMR). It made up 0.4% of the neutral substances.

The third fraction, consisting mainly of esters with small amounts of aldehydes and oxides, was treated with alcoholic alkali, and the acids were separated from the unsaponifiable substances. The unsaponifiable substances were separated on a column of silica gel into the alcohols produced by the saponification of the esters, methyl esters of resin acids, oxides, and aldehydes. The composition of the components of fraction 3 is given below (% on the fraction):

Acids	9.5
Unsaponifiables	87.1
Of them	
Alcohols	84.9
including	
borneol	0.3
geranyllinalool	0.1
geranylgeraniol	0.1
phytol	0.2
cycloartenol	1.0
24-methylenecycloartanol	2.0
citrostadienol	0.8
campesterol	Tr.
β-sitosterol	7.8
polyprenols	70.2
Aldehydes	1.5
including	

pimarinal	Tr.
isopimarinal	0.4
dehydroabietinal	0.5
abietinal	Tr.
neoabietinal	0.1
Oxides including	0.3
manoyl oxide	0.1
epimanoyl oxide	0.1
Esters of resin acids including	0.3
methyl isopimarate	0.1
methyl dehydroabietate	0.2
methyl abietate	Tr.
methyl neoabietate	Tr.

The aldehydes of fraction 3 (their composition was established after they had been converted into alcohols by reduction with sodium tetrahydroborate) consisted of compounds of the pimaric and abietic types. Isopimarinal and dehydroabietinal were the main components of the fraction (PMR, GLC). In addition to diterpene aldehydes, the fraction also contained small amounts of eight compounds of unknown structure (GLC).

Oxides were represented by seven components (GLC), of which the two main ones were isolated and identified with the addition of authentic samples of manoyl oxide and epimanoyl oxide (GLC) and also from their mass and PMR spectra.

The alcoholic component of the esters of the fraction consisted mainly of prenols, sterols, and triterpene alcohols. Borneol (0.3% of the neutral substances in fraction 3 and 1.1% in fraction 4) and the acyclic diterpene alcohols phytol, geranylgeraniol, and geranyllinancol were also identified.

The greatest interest is presented by the prenol fraction. Prenols are biologically active substances and are concentrated in the membranes of cells and, in phosphate form, effect the transport of carbohydrates from the corresponding nucleotide sugars for the synthesis of polysaccharides [16]. The use of some prenols for the treatment of ulcerous diseases of the stomach and duodenum and also of hypertension is known [17, 18].

It is known that in plants polyprenols are present in the form of esters with higher fatty acids [19] or acetic acid [20]. In order to isolate the acyl residues of the polyprenol esters, they were isolated by the method of repeated runs in TLC using as eluent petroleum ether with the addition of 0.5% of diethyl ether. It was established by spectral methods that in the extractive substances of the needles of the Norway spruce the polyprenols were present in the form of acetates (IR spectrum: 1740 and 1250 cm^{-1}; PMR spectrum 1.99 ppm, 3 H, singlet; 4.50 ppm, 2 H, doublet, J = 7.5 Hz ($C=C(H)-\underline{CH_2OAc}$)).

Geranyllinalool has been isolated previously from the oleooresin of the Siberian spruce [10] and the Norway spruce [21]. Geranylgeraniol has not previously been found in the genus Picea A. Ditr., but there is information on its isolation from the Siberian stone pine [22]. Phytol is a common component of the green parts of plants. It was isolated from an extract of Norway spruce needles as a component of the ester fraction and of the alcohol fraction.

Fraction 4 (see Table 1) consisted of triglycerides (1.2% on the neutral substances) and nonacosan-10-ol (0.8%). The borneol isolated from the same fraction was probably present in the form of an ester. The R_f value of borneol on TLC was smaller than that of fraction 4 before saponification. In the extractive substances of the spruce needles, nonacosan-10-ol is most probably present in the form of the alcohol, since the R_f value of fraction 4 before saponification and that of nonacosan-10-ol were identical.

The alcohols of the extractive substances of Norway spruce needles consisted of mono-, sesqui-, di-, and triterpene alcohols and sterols. The composition of the terpene alcohols was as follows (% on the neutral substances):

Borneol	1.0
α-Terpineol	0.3
δ-Cadinol	0.1

Phytol	0.5
Geranyllinalool	0.1
Epimanool	2.2
Epitorulosal	1.3
Isopimarinol	1.1
Dehydroabietinol	1.0
Abietinol	0.2
Neoabietinol	0.2
Cycloartenol	0.5
24-Methylenecycloartanol	1.5
β-Sitosterol	3.0
Campesterol	Tr.
Prenols	3.6.

The mono- and sesquiterpene alcohols were represented by borneol, α-terpineol, and δ-cadinol (GLC). Isopimarinol and dehydroabietinol were the main components of the tricyclic diterpene alcohols. Abietinol and neoabietinol were present in smaller amounts (GLC, PMR). The main component of the diterpene alcohols was bicyclic alcohol epimanool. cis-Abienol has been found previously in the olecresin of the Norway spruce [21], neoabienol and cembrene derivatives in the oleoresin of the Siberian stone pine, and phyllocladanol in the oleoresin of the Yeddo spruce [10]. We did not find these compounds in the alcohols of the extractive substances of the needles of the Norway spruce.

Phytosterols are common components of the extractive substances of various plants. Among the sterols we identified sitosterol and campesterol, and from the triterpene alcohol fraction we isolated cycloartenol and 24-methylenecycloartanol (PMR). These compounds were present both in the form of the alcohols and also in the form of esters. Citrostadienol was isolated only from the fraction of esters after their saponification.

From fraction 8, after its acetylation and chromatography on a silica gel column, a compound was isolated the PMR spectrum of which coincided in the low-field region with that of epimanool. In the high-field region the PMR spectra differed. The spectrum of the compound isolated lacked the signal of one methyl group and showed the signals of methylene protons appearing in the form of an AB system with components at 3.63, 3.82, 4.07, and 4.25 ppm and also the signal of an acetate group (1.90 ppm, 3 H, singlet). The signals of methylene protons in the 3.63-4.25 ppm region are characteristic for an axial $-CH_2O$ group, while in the case of the equatorial position the signals of the methylene protons are present in a strongest field [22]. The general form of the spectrum made it possible to assume that the compound isolated was epitorulosol acetate. Epitorulosol is one of the main components of the oleoresin of some species of the genus Larix and, in particular, of the Siberian larch Larix sibirica Ledeb. [23, 24]. We have found no reports in the literature on the isolation of epitorulosol from species of the genus Pices A. Ditr.

EXPERIMENTAL

PMR spectra were recorded on a Varian A 56/60A instrument for solutions in carbon tetrachloride (with HMDS as internal standard) and a Bruker WP-200 instrument for solutions in deuterochloroform (with TMS as internal standard), δ scale. IR spectra were obtained on a UR-20 instrument. The composition of the terpenes was determined on a Chrom-41 chromatograph with a capillary steel column 50 m long and 0.25 mm in internal diameter containing the stationary phase OV-225 in a stream of nitrogen as the carrier gas with programming of the temperature from 100 to 190°C at a rate of heating of the thermostat of 2°C/min.

For adsorption chromatography we used air-dry silica gel (100-160, Czechoslovakia) with, as eluent, petroleum ether (bp 40-70°C) containing increasing amounts (up to 100%) of diethyl ether. Separation was monitored by TLC on Silutol plates or by GLC.

The place and time of collecting the sample of Norway spruce needles, the conditions of extraction and of the saponification of the esters, and also the group composition of the extracts have been given in [25].

Analysis of the Hydrocarbons. Fraction 1 was separated by column chromatography on silica gel with 5% of silver nitrate. Petroleum ether eluted alkanes and petroleum ether containing 3% of diethyl ether eluted the combined mono- and sesquiterpenes. The substances eluted from the column and having on TLC R_f values close to those of samples of isopimaradiene and cembrene were collected separately. The terpene hydrocarbons were identified by GLC.

Fraction 2, likewise containing hydrocarbons, was analyzed by GLC. The chromatogram had seven peaks the main component of the fraction coinciding with a sample of the triterpene hydrocarbon squalene. The latter was isolated from the fraction on a column of silica gel containing 5% of silver nitrate with petroleum ether containing 30% of diethyl ether. The remainder of the fraction was dark red in color and probably contained carotenoids. No identification of the carotenoids was carried out.

Squalene. PMR spectrum (carbon tetrachloride, 60 MHz, ppm): 1.58 (18 H, singlet, 6 trans-CH_3); 1.66 (6 H, singlet, terminal 2 cis-CH_3); 2.03-2.11 (20 H, the signals of $-CH_2-CH_2-$ fragments); 5.13 (6 H, broad unresolved multiplet, $C=CH-$ groups).

Isolation of the Main Groups of Compounds from the Ester Fraction. Fraction 3 (9.3 g) was saponified with a 0.5 N solution of potassium hydroxide in ethanol for 20 min and it was then separated into acids (9.5% on fraction 3) and unsaponifiable substances (87.1%). It was established by TLC that the unsaponifiable substances consisted of two groups. The first group of substances had the same R_f value as the whole of fraction 3 before saponification and consisted of aldehydes, oxides, and methyl esters of resin acids. The second group of substances gave a series of spots on a chromatogram with R_f values smaller than that of the ester fraction before saponification. The first group of substances was separated on a column of silica gel using petroleum ether with 5% of diethyl ether as eluent. The second group of substances – the products of the saponification of the ester – was separated into three fractions. A fraction eluted from a silica gel column by petroleum ether containing 10-12% of diethyl ether contained mainly prenols; with the addition of 20-40% of diethyl ether, triterpene alcohols were obtained, and with 40-60% of diethyl ether, sterols. The separation of 8.02 g of unsaponifiable substances gave 0.27 g of a first group of substances and 7.66 g of a second group including 6.03 g of a prenol fraction, 0.58 g of triterpene alcohols, and 1.05 g of sterols.

Separation of the Prenol Fraction. The prenols were freed from accompanying substances in the following way. The fraction (6.00 g) was acetylated with acetic anhydride in pyridine and the resulting acetates were separated from the unacetylatable part on a column of silica gel. Petroleum ether containing 5% of diethyl ether eluted alcohol acetates, and petroleum ether containing 10% of diethyl ether eluted as alcohol, which was identified as geranyllinalool. Chromatography of the alcohol acetates on a column containing silica gel + 5% of silver nitrate led to the isolation of borneol acetate (petroleum ether containing 5% of diethyl ether), phytol acetate (petroleum ether with 12% of diethyl ether), geranylgeraniol acetate (with 30% of diethyl ether), and prenol acetates (with 80% of diethyl ether).

Geranyllinalool: 0.018 g, oil, PMR spectrum (60 MHz, carbon tetrachloride, ppm): 1.20 (3 H, singlet, $-C(OH)-CH_3$); 1.58 (9 H, singlet, 3–$C(CH_3)=C$); 1.63 (3 H, singlet, one of the terminal methyl groups); 2.00-2.05 (12 H, multiplet, 3 $-CH_2-CH_2-$); 4.96 (1 H, doublets of doublets, J = 10.5 and 2.0 Hz) and 5.15 (1 H, doublet of doublets, J = 18.5 and 2.0 Hz, $C=CH_2$); 5.85 (1 H, doublet of doublets, J = 18.5 and 10.5 Hz, $-CH=CH_2$); and 5.09 (3 H, multiplet, $-C(CH_3)=CH-$). $[\alpha]_D^{24}-12.1°$ (c 0.2; chloroform): according to the literature [21]: $[\alpha]_D$ −10.2° (c 1.2; chloroform).

Phytol acetate: 0.04 g, PMR spectrum (60 MHz, carbon tetrachloride, ppm): 0.85-0.92 (12 H, singlets, tertiary methyl groups); 1.25-1.30 (16 H, singlets, 8 $-CH_2-$); 1.74 (3 H, singlet, $C(CH_3)=CH-CH_2-$); 2.08 (5 H, singlets from the protons of an acetate group and multiplet from a $-CH_2-C=C-$ fragment), 5.48 (1 H, triplet, J = 7 Hz, $-C=CH-CH_2O-$); and 4.70 (2 H, doublet, CH_2O-). After the saponification of the phytol acetate and the usual working up, a compound was obtained the PMR spectrum of which was similar to that of phytol [25].

Polyprenol acetates: 5.4 g, oil, PMR spectrum (200.13 MHz, deuterochloroform, ppm): 1.56 (12 H, singlet, 4 trans-CH_3); 1.65 (42 H, singlet, 14 cis-CH_3); 1.74 (3 H, singlet, $-C(CH_3)=CH-CH_2O-$); 1.95-2.05 (71 H, $-CH_2OAc$ and $-CH_2-CH_2-$); 4.50 (2 H, doublet, J = 7 Hz, $-CH_2OAc$); 5.08 (17 H, broad unresolved multiplet, $-C(CH_3=CH-$); and 5.31 (1 H, triplet, $-C=CH-CH_2O$).

Isolation of Polyprenol Esters from the Ester Fraction. The ester fraction (0.12 g) isolated from an individual portion of the extract was separated by GLC on Silufol plates with 8-10 runs in petroleum ether containing 1% of diethyl ether. The largest spot on the chromatogram having a R_f value smaller than that of β-sitosterol acetate (marker) was scraped

off the main part of the plate and the substance was eluted from the silica gel with diethyl ether. The separation of the fraction and the positions of the polyprenol ethers were monitored by cutting off lateral strips of the plates and spraying them with sulfuric acid. In this way, 0.04 g of compounds the PMR spectrum of which was identical with that of synthetic polyprenol acetates was obtained.

Separation of the Components of the Triterpene Alcohols and Sterols from the Unsaponifiable Part of Fraction 3. The fraction eluted from the column after the polyprenols (0.58 g) was acetylated with acetic anhydride in pyridine and was separated on a column of silica gel + 20% of silver nitrate. Petroleum ether containing 3% of diethyl ether eluted successively the acetates of higher fatty alcohols, cycloartenol acetate (0.1 g), 24-methylenecycloartanol acetate (0.2 g), and citrostadienol acetate (0.08 g), and petroleum ether with 20% of diethyl ether eluted geranylgeraniol acetate (0.015 g). The acetates of cycloartenol, of 24-methylenecycloartanol, and of geranylgeraniol were identified by comparing the PMR spectra of the compounds isolated and of standard compounds, and also by TLC and GLC.

Citrostadienol acetate: mp 149.5-150°C; PM spectrum (200.13 MHz, deuterochloroform, ppm): 0.52 (3 H, singlet), 0.82 (3 H, singlet), 0.82 (3 H, singlet), 0.83 (3 H, doublet, J = 6.0 Hz), 0.93 (3 H, doublet, J = 6.0 Hz), 0.95 (6 H, doublet, J = 7.0 Hz), and 1.58 (3 H, doublet J = 6.5 Hz), methyl groups; 2.03 (3 H, singlet, $-CHOAc$); 2.81 (1 H, septet, J = 7.0 Hz, $-CH(CH_3)_2$); 4.50 (1 H, multiplet, $CH-OAc$); 5.08 (1 H, quartet, J = 6.5 Hz, $C=CH-CH_3$); and 5.16 (1 H, multiplet, $C=CH-$). Chloroform was used as the internal standard, its signal being taken as 7.24 ppm. According to the literature [26]: mp 148-150°C.

The sterol fraction contained 95% of β-sitosterol, 2.5% of campesterol, and 2.5% of an unidentified component (GLC and chromato-mass spectrometry).

The first group of substances isolated from the unsaponifiables of fraction 3 was reduced with sodium tetrahydroborate in ethanol [27]. The alcohols obtained from the reduction of the aldehydes were separated from the unreducible part of the fraction on a column of silica gel. The yield of alcohols from the reduction of aldehydes was 0.16 g. Their composition was established from their PMR spectrum and by GLC.

Determination of the Composition of the Methyl Esters of Resin Acids and Oxides. A portion of that part of the fraction that was not reducible by sodium tetrahydroborate was analyzed by GLC with the addition of the markers manoyl oxide, epimanoyl oxide, and methyl esters of resin acids. The analysis was performed in a glass column containing 3% of SE-30 on Inerton-super, with programming of the temperature from 130 to 210°C at the rate of 6°C per minute. For the additional identification of the components, the residue of the fraction (100 mg) was reduced with lithium tetrahydroaluminate in diethyl ether [27] and the reduction products were separated from the unreducible part on a column of silica gel. This gave 70 mg of unreduced compounds and 25 mg of alcohols resulting from the reduction of resin acid methyl esters. The compositions of the fractions isolated were confirmed from their PMR spectra in comparison with the spectra of manoyl oxide, epimanoyl oxide, and diterpene alcohols.

Determination of the Composition of the Alcohols. The compositions of the alcohols in all the fractions (beginning with the fifth) were studied by a single scheme [27]. The fractions were acetylated with acetic anhydride in pyridine (20 h at room temperature), and the resulting acetates were separated from the unacetylatable part of the fraction on a column of silica gel. The fractions isolated were separated into individual components or groups of substances by rechromatography on silica gel with the addition of from 5 to 20% of silver nitrate.

Isolation and Identification of the Components of Fraction 5. After the acetylation and the appropriate working up of the fraction, saponification on a column of silica gel yielded 1.1 g of alcohol acetates and 0.5 g of unacetylatable tertiary alcohols. From the alcohol acetate fraction by chromatography on a column of silica gel with the addition of 5% of silver nitrate were isolated borneol acetate (5% of diethyl ether in petroleum ether, identification by TLC and GLC with a standard sample of borneol acetate), phytol acetate (10% of diethyl ether in petroleum ether; identification by a comparison of the PMR spectrum of the compound isolated from fraction 5 and that of the phytol acetate from fraction 3, and also by TLC and GLC with a standard sample of phytol acetate), and prenol acetates (0.81 g; eluent: 80% of diethyl ether and 20% of petroleum ether, identification by PMR spectroscopy).

From the tertiary alcohol fraction by chromatography on a column of silica gel with the addition of 10% of silver nitrate were isolated epimanool (petroleum ether containing 18% of diethyl ether) and geranyllinalool (30% of diethyl ether in petroleum ether: identification by PMR and also by TLC and GLC with an authentic sample of geranyllinalool).

Epimanool. This was obtained in the form of an oil, 0.46 g, $[\alpha]_D^{22}$ + 49.8° (c 3.6; chloroform). According to the literature [28]: $[\alpha]_D$ + 48° (chlf).

Isolation and Identification of the Components of Fraction 6. After the acetylation of fraction 6 (1.87 g) and column chromatography, two fractions were obtained which consisted of the acetates of higher fatty, diterpene, and triterpene alcohols (1.64 g) and of tertiary alcohols incapable of being acetylated under the given conditions (0.12 g). The latter consisted of δ-cadinol (0.02 g) and α-terpineol (0.08 g). They were identified by GLC and TLC with authentic samples and, in the case of α-terpineol, by PMR.

GLC of the acetate fraction established qualitatively and quantitatively the presence of acetates of di- and triterpene alcohols (GLC conditions: 3% of SE-30 on Inerton-super with programming of the temperature from 130 to 270°C, at a rate of heating of 6°C/min). By column chromatography of the acetates on silica gel with the addition of 10% of silver nitrate the acetates of higher fatty alcohols (0.64 g), dehydroabietinol acetate (0.20 g), cyclocartemol acetate (0.10 g), 24-methylenecycloartanol acetate (0.31 g), and isopimarinol acetate (0.18 g) were eluted successively. The components isolated were identified from their PMR spectra.

Analysis of Fraction 7. After the saponification of fraction 7 (0.90 g) with alcoholic alkali and appropriate working up, acids (0.12 g) and unsaponifiable substances (0.65 g) were obtained. The unsaponifiable substances consisted of β-sitosterol (97%) and campesterol (3%) (GLC of the corresponding acetates with 3% of SE-30 on Inerton-super with programming of the temperature from 190 to 270°C at a rate of heating of 6°C/min). Since the unsaponifiable substances of fraction 7 consisted only of sterols which did not change their R_f values after the saponification of the fraction (TLC), it may be assumed that the acids were formed by the saponification of diglycerides.

The polar fractions of neutral substances eluted from the column after the sterol fractions were acetylated, and from the acetates epitorulosol acetate was isolated. The remainder of the fraction consisted of chlorophyll derivatives and wax-like products.

SUMMARY

The composition of the petroleum-ether-soluble neutral components of an isopropanol extract of the needles of the Norway spruce Picea abies (L.) Karst. has been studied. The compositions of the hydrocarbons, aldehydes, oxides, esters, and alcohols have been established. The main components of the terpenoids are prenol acetates, sterols, and triterpene alcohols, and also epimanool and derivatives of isopimarene and of dehydroabietadiene.

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CIRCULAR DICHROISM OF SOME SESQUITERPENE LACTONES OF THE GERMACRANE TYPE

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The CD spectra of a series of germacranolides have been considered, and the parameters of the Cotton effects observed have been correlated with the stereochemistries of the compounds studied. The applicability for germanocranolides of the Waddell–Stocklin–Geissman rule is discussed.

The empirical rules used for determining the stereochemistry of the lactone ring in sesquiterpenoids such as Samek's rule in NMR spectroscopy [1, 2] or the Waddell–Stocklin–Geissman rule in CD spectroscopy [3] do not always give correct information.

Cases of anomalous behavior have been reported among the guaiane and eudesmane lactones, but they are particularly numerous in the germacranolide series, which is due to the high conformational flexibility of the germacrane skeleton.

In order to correlate features of the spatial structures of the germacranolides with the parameters of their Cotton effects, we have considered the CD spectra of a number of lactones: tanachin (I), tamirin (II), tavalin (III), deacetyllaurenobiolide (IV), mucrin (V), dihydromucrin (VI), mucronin (VII), and balchanolidè (VIII), and a bislactone – mycoguaianolide (IX), the structures of which have been described previously [4-7].

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