O-ACYLATED LIGNANS FROM THE WOOD OF Abies SPECIES

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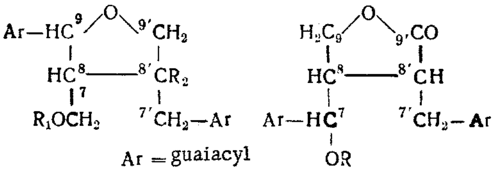
UDC 547.639 : 634.866

We have previously [1, 2] reported the isolation from extracts of the wood of the Siberian fir and the Khingan fir of previously unknown O-acyl derivatives of lignans – laricyl coumarate and laricyl ferulate. Having continued the study of the composition of the phenolic compounds of the wood of Abies species, as the result of a quantitative accumulation of the chloroform fraction obtained from the acetone extract [1], we have isolated another five new compounds (I-V), the amount of which in the initial extract is very low. The names of these compounds and the numbering of the atoms are given in agreement with the Freudenberg and Weinges classification of lignans [3].



I, II, III IV, V

I – 4,4'-dihydroxy-3,3'-dimethoxy-9-vanilloyloxy-7,9'-epoxylignan; R_1 = vanilloyl; R_2 = H;
II – 9-coumaroyloxy-4,4',8'-trihydroxy-3,3'-dimethoxy-7,9'-epoxylignan; R_1 = coumaroyl; R_2 = OH;
III – 9-feruloyloxy-4,4',8'-trihydroxy-2,3'-dimethoxy-7,9'-epoxylignan; R_1 = feruloyl; R_2 = OH;
IV – 4,4'-dihydroxy-7-(4"-hydroxybenzoyloxy)-3,3'-dimethoxy-9,9'-olide; R = p-hydroxybenzoyl; and
V – 4,4'-dihydroxy-3,3'-dimethoxy-7-vanilloyloxylignan-9,9'-olide; R = vanilloyl.

The basic approach to determining the structures of the compounds isolated was similar to that described previously [2].

After alkaline hydrolysis it was found that all the compounds were esters in which the acyl radicals consisted of residues of p-hydroxybenzoic acid (compound IV), vanillic acid (I, V), p-coumaric acid (II) or ferulic acid (III), and the role of the alcohol radicals was fulfilled by the lignans lariciresinol (I) and olivil (II, III), belonging to the group of guaiamonoepoxylignans, and hydroxymatairesinol (IV, V), which is a guaialignanolide.

The ester natures of these compounds were confirmed by IR and UV spectroscopy. The IR spectra of compounds (I-III), unlike the IR spectra of lariciresinol and olivil [1] show the bands of the stretching vibrations of a carbonyl group in the 1702-1712 cm^{-1} region. In the hydroxymatairesinol derivatives, in addition to the band at 1760 cm^{-1} corresponding to the carbonyl of the lactone ring [1], a band is observed in the 1708-1712 cm^{-1} region which is due to the carbonyl group of an ester grouping.

The above-mentioned phenolic acids were identified by the GLC of their TMS ethers [4], and the lignans by their physicochemical constants, spectral characteristics, and chromatographic behavior.

The position of O-acylation of lariciresinol by p-coumaric or ferulic acid was reliably determined by a comparative study of the behavior of the phenolic and aliphatic hydroxy groups in the initial and isolated lignans

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Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 337-341, May-June, 1977. Original article submitted February 24, 1977.

by IR and PMR spectroscopy using the semisynthesis of individual models [2]. In this connection, in the present work it proved to be sufficient to perform a comparative analysis of IR spectroscopic characteristics in order to determine the positions of the acyl residues in the lignans.

It may be assumed that in compounds (I)-(V) the aliphatic hydroxy groups undergo esterification. Thus, in the IR spectra of (I-V) taken in chloroform at high dilution the absorption band of free phenolic hydroxy groups can be detected in the 3550-3560 cm^{-1} region coinciding with the absorption band of these hydroxyls in the initial lignans.

In lariciresinol, there is one primary alcohol group the absorption bands of which are not present in the IR spectrum of compound (I). However, in the lignin obtained after hydrolytic cleavage of the ester a band corresponding to the vibrations of this group (3640 cm^{-1}) appears clearly. This shows that it is just the alcoholic group of lariciresinol that takes part in esterification with phenolic acids.

As in the case considered, in the IR spectra of compounds (IV) and (V) there are no bands corresponding to the vibrations of a secondary alcoholic hydroxyl, but such bands appear in the hydroxymatairesinol liberated by hydrolyxix (3630 cm^{-1}).

Olivil, which is present in the esters (II) and (III), has two hydroxy groups – primary and tertiary alcoholic. The choice between them was again made with the aid of IR spectroscopy. Thus, in the IR spectra of compounds (II) and (III), in addition to the absorption band of aromatic hydroxygroups (3550 cm^{-1}) there is a band (3615 cm^{-1}) corresponding to a tertiary alcohol group. As a result of the cleavage of these ester derivatives, the band of a primary alcoholic hydroxyl appears in the IR spectrum at 3640 cm^{-1}. This permits us to consider that the esterification of olivil took place at the primary alcohol group.

Thus, in the wood of the Siberian fir and the Khingan fir a new group of lignin derivatives have been detected – esters of lignins with phenolic acids. It may be mentioned that the two related guaiamonoxylignans – lariciresinol and olivil – are esterified at the primary alcoholic hydroxyl by hydroxycinnamic acids – p-coumaric or ferulic acid. For lariciresinol a derivative with vanillic acid has been found. The representative of the guaialignanolides – hydroxymatairesinol – is esterified at the secondary alcoholic hydroxyl with p-hydroxybenzoic or vanillic acid. Here the acids of the hydroxybenzoic and hydroxycinnamic types taking part in esterification are analogs of the model of substitution of the benzene ring.

EXPERIMENTAL

The UV spectra were taken in ethanol on a Unicam-SP-8000 recording spectrophotometer and the IR spectra of the substances were taken in KBr and in chloroform at a concentration of 0.001 M with dilution. Gas-liquid chromatography (GLC) was performed on a Tsvet-4 chromatograph with a flame-ionization detector using a column 300 × 0.3 cm filled with 5% of SE-30 on Chromaton N-AW-HMDS with helium as the carrier gas and a temperature of the column of 215°C and of the evaporator of 320°C.

Compounds (I-V) were isolated by preparative column chromatography on silica gel impregnated with 2% of sodium metabisulfite [eluent chloroform–acetone (9 : 1)], and they were additionally purified by chromatography on a LH-20 instrument [eluent hexane–ethyl acetate (6 : 4)].

The purity of the compounds was checked by thin-layer chromatography on impregnated silica gel in solvent system 1 [chloroform–methanol (8 : 2)].

The phenolic acids obtained by the alkaline saponification of (I)-(V) were analyzed in the form of the trimethylsilyl (TMS) ethers by the GLC method (RRTs of the TMS ethers: p-coumaric 1.62; ferulic 2.48; vanillic 0.78; p-hydroxybenzoic 0.52).

Treatment of the Extract. Acetone extracts of the woods were fractionated by a method described previously [2].

Alkaline Saponification was performed under the conditions described previously [2].

Substance (I) was an amorphous powder with a softening temperature of 81-83°C, R_f 0.5 [system 1, chloroform–ethyl acetate (3 : 2)]. UV spectrum: λ_{max} 231, 265, 287 nm (log ε 4.31, 4.19, 3.98). IR spectrum (KBr), cm^{-1}: 3510 (assoc OH); 2850 (OCH_3); 1712 (C = O of an ester group); 1603, 1510, 1432 (C_6H_5); 1270, 1240, 1035 (C–O–C) [chloroform, c 0.001 M with dilution, 3555 cm^{-1} (assoc. arom. OH)]. The alkaline hydrolysis of (I) formed lariciresinol with mp 167-168°C (methanol) and other constants corresponding to those given previously [1], and vanillic acid with mp 206-207°C (ether).

Substance (II) formed an amorphous powder with a softening temperature of 92-94°C, R_f 0.25 (system 1). UV spectrum: λ_{max} 232, 289, 318 nm (log ε 4.39, 4.21, 4.09). IR spectrum (KBr), cm^{-1}: 3450 (assoc OH); 2865 (OCH_3); 1712 (C=O of an ester group); 1605, 1510, 1430 (C_6H_5); 1270, 1230, 1030 (C−O−C); [chloroform, c 0.001 M with dilution, 3550 cm^{-1} (assoc. arom. OH)]; 3615 (tert. OH).

The alkaline hydrolysis of (II) formed olivil with mp 119-120°C (methanol) [1], and ferulic acid with mp 171-172°C (methanol).

Substance (III) formed an amorphous powder with a softening temperature of 89-91°C, R_f 0.4 (system 1). UV spectrum: λ_{max} 231, 287, 332 nm (log ε 4.25, 3.89, 3.75). IR spectrum (KBr), cm^{-1}: 3410 (assoc. OH); 2860 (OCH_3); 1702 (C=O of an ester group), 1613, 1518, 1435 (C_6H_5); 1275, 1240, 1035 (C−O−C) [chloroform, c 0.001 M with dilution, 3550 cm^{-1} (assoc. arom. OH)]; 3615 (tert. OH).

The alkaline hydrolysis of (III) formed olivil with mp 119-120°C (methanol) [1] and ferulic acid with mp 171-172°C (methanol).

Substance (IV) formed an amorphous powder with a softening temperature of 66-68°C, R_f 0.8 (system 1). UV spectrum: λ_{max} 232, 260, 290 nm (log ε 4.40, 4.21, 4.03). IR spectrum (KBr), cm^{-1}: 3440 (assoc. OH); 2850 (OCH_3); 1708 (C=O of an ester group); 1760 (C=O of a lactone ring); 1605, 1518, 1432 (C_6H_5); 1275, 1240, 1040 (C−O−C) [chloroform, c 0.001 M, with dilution, 3560 cm^{-1} (assoc. arom. OH)].

The alkaline hydrolysis of (IV) formed hydroxymatairesinol with mp 124-125°C (benzene) [1] and p-hydroxybenzoic acid with mp 208-209°C (hexane−ether).

Substance (V) formed an amorphous powder with a softening temperature of 71-73°C, R_f 0.7 (system 1). UV spectrum: λ_{max} 233, 265, 287 nm (log ε 4.32, 4.18, 4.01). IR spectrum (KBr), cm^{-1}: 3445 (assoc. OH); 2850 (OCH_3); 1712 (C=O of an ester group); 1765 (C=O of a lactone ring); 1608, 1515, 1430 (C_6H_5); 1270, 1230, 1035 (C−O−C) [chloroform, c 0.001 M, with dilution, 3560 cm^{-1} (assoc. arom. OH)].

The alkaline hydrolysis of (V) formed hydroxymatairesinol with mp 124-125°C (benzene) [1] and vanillic acid with mp 206-207°C (ether).

IR spectra of the lignans (region of OH groups; chloroform, c 0.001 M with dilution), cm^{-1}: lariciresinol − 3550 (assoc. arom. OH), 3640 (primary OH); olivil − 3545 (assoc. arom. OH), 3615 (tert. OH), 3640 (prim. OH); hydroxymatairesinol − 3550 (assoc. arom. OH), 2630 (sec. OH).

SUMMARY

From the wood of the Siberian fir Abies sibirica Ledeb. and the Khingan fir A. nephrolepis Maxim., five new compounds have been isolated which are ester derivatives of the lignans lariciresinol, olivil, and hydroxymatairesinol.

It has been established that olivil is esterified at the primary alcoholic hydroxyl by hydroxycinnamic acids − p-coumaric or ferulic − and lariciresinol is esterified by vanillic acid. A representative of the guaialignanolides − hydroxymatairesinol − is esterified at the secondary aliphatic hydroxy group with p-hydroxybenzoic or vanillic acid.

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