## ALKYL FERULATES FROM THE BARK AND WOOD OF PLANTS OF THE PINACEAE FAMILY

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Ferulic acid is widely distributed in coniferous plants both in the free state and in the form of esters with aliphatic alcohols. Alkyl ferulates are contained more frequently and in larger amount in the bark [1-3] than in the wood [4].

From acetone extracts of the bark of the Siberian pine and of the Khingan fir, and also from the wood of the Korean spruce and the Siberian fir by successive treatment with solvents of increasing polarity we have isolated a fraction of nonpolar substances. By chromatography on silica gel and alumina, two groups

TABLE 1. Alkyl Radicals in the Ferulic Acid Esters

Rad- ical	RRT*	Bark, %			Wood, %	
		Siberian pine	Scotch pine	Khingan fir	Siberian spruce	Siberian fir
C <sub>16</sub> C <sub>17</sub> C <sub>18</sub>	0,34 0,46 0,60	Traces	Traces	Traces	Traces	 Traces
$C_{19} \\ C_{20}$	0,80 1,0	0,5 0,5	0,2 3,5	0,1 0,1	0,4 0,8	0,2 0,1
$C_{21}$	1,3	Traces				
$C_{22}^{22}$	22	Traces	Traces	0.1	0.4	0.3
$C_{24}^{23}$	2,9	81,0	17,6	85,0	57,0	74,0
C25	3,8	Traces	Traces	0,2	-	-
Can	1 50	1 0.5	1 08	1 0.3		

\*Relative retention time.



Fig. 1. Relationship between the logarithms of the retention times (log RT) and number of carbon atoms in the n-alcohols (Cn).

of alkyl ferulates showing the cis and trans isomerism of the ferulic acid esters have been isolates from this fraction.

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By the alkaline hydrolysis of the esters  $[\nu_{\rm CO} 1710 \text{ cm}^{-1} \text{ (cis)} \text{ and } 1720 \text{ cm}^{-1} \text{ (trans)} \text{ in}$  the IR spectra with KBr] with 5% KOH in methanol we obtained ferulic acid, which was identified in the form of the TMS ester by GLC under the conditions described previously [5]. The ferulic acid isolated preparatively was identified from its IR and UV spectra and by a mixed melting point with an authentic sample.

The neutral fraction of the hydrolyzate was analyzed by GLC with the stationary phase 5% E-30 on Chromaton N-AW-HMDS. Tsvet-4 chromatograph with a flame-ionization detector, column 300 × 0.3 mm, column temperature 260°C, carrier gas helium (1 atm), rate of flow of hydrogen, 1.75 liter/h, rate of flow of air 17.5 liters/h.

The alcohols were identified by comparing their retention times (RTs) with those of authentic samples, and for the alcohols that were not available we used the linear relationship between the logarithms of the RTs and the number of carbon atoms in the alcohol (Fig. 1). Quantitative analysis was performed by internal normalization from the area of the peaks (Table 1). As

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can be seen from the Table, the neutral fraction is represented by a large variety of alcohols with numbers of carbon atoms from  $C_{16}$  to  $C_{26},$  but the bulk is represented by the  $C_{22}$  and  $C_{24}$  alcohols.

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