

# Reactions of bromotrimethylsilane with lignin and lignin model compounds

S. M. SHEVCHENKO, L. G. AKIM, A. G. APUSHKINSKY, and V. A. GINDIN

*Leningrad Forest Technical Academy, SU-194018 Leningrad*

Received 15 September 1989

Bromotrimethylsilane reacts with *p*-hydroxybenzyl alcohols, *p*-hydroxystyrenes and related quinone methides, respectively giving *p*-hydroxy- $\alpha$ -bromides.  $\alpha$ -Bromides are formed also when a phenol hydroxy group is protected. Milled wood lignin (black spruce) added to bromotrimethylsilane in dioxane solution gives a product containing about 20 % of bromine in a side chain, but no silicon.

Bromotrimethylsilane (BTMS) is a well known reactant for transformation of lignin model *p*-hydroxybenzyl alcohols into corresponding *p*-quinone methides [1]. This reaction is usually regarded as a one-flask synthesis, and no intermediate bromides have been characterized yet. It was also interesting to testify, whether *p*-hydroxystyrenes could react in a similar manner. Another problem is the reaction of BTMS with lignin itself: the results of model experiments have led to the conclusion that this reaction might be useful in lignin selective transformation.

## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC 200 spectrometer at 295 K. For the lignin model compounds, the spectra were determined in CDCl<sub>3</sub> with TMS as internal reference substance, for the samples of lignin in DMSO-d<sub>6</sub> (4 % solutions) with a signal of residual DMSO as internal standard. Elemental microanalyses were performed using standard equipment in a period of 1—3 days after syntheses of the samples 1, 3—6 (Table 3). With the aim to check how stable are some lignin derivatives, we repeated elemental microanalyses of the sample 1 one month later; this partly decomposed substance is referred to as the sample 2.

Lignin model compounds *I*, *IVc*, *VIIb*, *XI* (see Schemes) were synthesized according to literature [2, 3]; some of them (*IVb*, *VIIa*, *VIII*, *X*) were of commercial origin. The transformation of bromides *II* into quinone methides *III*, and of the latter into *p*-hydroxystyrenes *IV* has been described elsewhere [1, 4, 5]. Isomerization of the quinone methide *XIII* into corresponding styrene *XIV* has been carried out in similar conditions (1.5 h, 50°C, CDCl<sub>3</sub>).

All the bromides were prepared by a treatment of starting compounds (30 mg) in CDCl<sub>3</sub> (1 cm<sup>3</sup>) with BTMS (3 equivalents) for 1—5 min. In a course of consequent

experiments the solutions were shaken with saturated aqueous solution of sodium hydrogen carbonate, and the chloroform layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The spectra were recorded immediately after the syntheses. *p*-Hydroxybenzyl bromides are stable in solutions at room temperature, but decompose during attempts to obtain them individually even in mild conditions. Therefore these compounds are characterized only by spectroscopic methods.

Milled wood lignin (MWL) of black spruce was prepared according to [6] and dried in a desiccator with  $\text{P}_2\text{O}_5$ . In the repeated experiments with MWL we treated the initial substance with the reactants to demonstrate reproducibility. To prepare the samples 1—4, MWL (50 mg) was dissolved in anhydrous 1,4-dioxane ( $2\text{ cm}^3$ ) and added to a solution of BTMS (40 mg) in the same solvent ( $2\text{ cm}^3$ ) under stirring. The mixture was poured out into an excess of pentane 72 h after. The precipitated product was separated, washed with pentane and dried in a vacuum desiccator. Methoxyl groups content determined for one of the samples is practically unchanged after the treatment of MWL with BTMS, being equal to 0.9 per phenylpropane unit. As it was pointed out, we describe the sample 1 after one month keeping at room temperature as the sample 2.

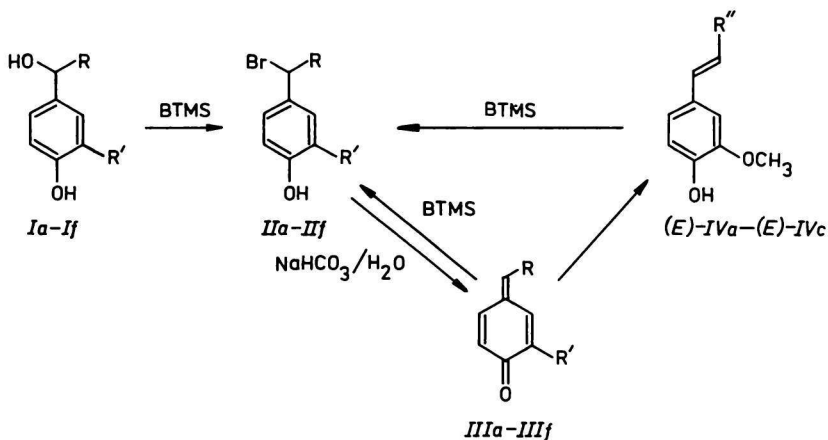
To prepare the samples 5 and 6, MWL (60 mg) was dissolved in anhydrous dioxane ( $2\text{ cm}^3$ ), and then dry HBr was bubbled through the solution during 15 (sample 5) or 20 (sample 6) min. As a result, a jelly solid precipitated. The mixture was mixed with an excess of hexane 24 h after, then the solvent evaporated under a low pressure, and the sample was dried in a vacuum desiccator.

## Results and discussion

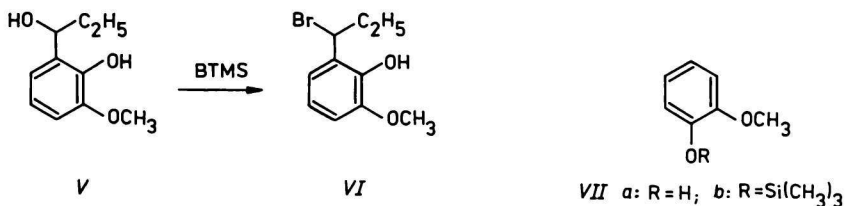
Solutions of *p*-hydroxybenzyl alcohols *I* were treated with an excess of BTMS to give bromides *II* which might be converted easily into corresponding quinone methides *III* [1, 5]. The  $^1\text{H}$  NMR spectra (Table 1) of bromides are very characteristic and demonstrate typical consequences of a change of the  $\alpha$ -hydroxy group for the bromine atom. Really, the fact of substitution of the  $\alpha$ -hydroxy group for bromine atom gives rise to no doubt because it has been shown earlier that tertiary and benzyl alcohols in  $\text{CHCl}_3$  give corresponding bromides with BTMS fast and quantitatively at room temperature [7].

$^1\text{H}$  NMR spectroscopy is not appropriate for determining whether the phenol hydroxy group is silylated or not, because there is a lot of intense signals in high fields. But it is necessary to say that in all the cases under consideration there were no signals in the region of  $\delta = 0.06\text{--}0.35$  which might be ascribed to trimethylsilyloxy groups of the bromides obtained, according to the intensities of these signals (the signal of trimethylsilyloxy group of the compound *VIIb* is observed at  $\delta = 0.17$ ).  $^{13}\text{C}$  NMR data (Table 2) demonstrate no significant displacement of the signals of carbons of  $\text{C}_{\text{arom}}\text{—O}$  as a result of the treatment of the compounds *Ib* and *XI* with BTMS (*cf.* *VIIa* and *VIIb*). Therefore we can ascribe the structure of *p*-hydroxybenzyl bromides *II* to the products.

It seems that a mechanism of the reaction between alcohols *I* and BTMS may include a formation of benzyl cation or, alternatively, be regarded as 1,6-addition of HBr to transient quinone methide *III* (it has been shown that the latter may be converted easily into bromide *II* with BTMS). Anyway, in the reaction with alcohols *I* BTMS acts as a mild brominating agent only, and it is not quite clear, whether BTMS reacts itself or dry HBr is formed (presented necessarily), that converts alcohols into bromides (Scheme 1).



	a	b	c	d	e	f
For <i>I-III</i>						
R:	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> (2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )	CH(CH <sub>3</sub> )O(2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )
R':	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	OCH <sub>3</sub>	H	OCH <sub>3</sub>
For <i>IV</i>						
R'':	H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>			



Scheme 1

Table 1

<sup>1</sup>H NMR data ( $\delta(J/\text{Hz})$ ) of lignin model compounds

Compound	OCH <sub>3</sub> (or OCH <sub>2</sub> O)	Ar (or QM)	$\alpha$ -CH	R
<i>Ia</i>	3.92	6.80 7.00	4.85 q (6.5)	1.49 d (6.5)
<i>IIa</i>	3.94	6.70 7.00	5.24 q (6.7)	2.04 d (6.7)
<i>Ib</i>	3.90	6.75 6.95	4.51 t (6.8)	0.90 t (7.0), 1.80 m <sup>u</sup>
<i>IIb</i>	3.93	6.80 6.95	4.89 t (7.7)	1.01 t (7.3), 2.24 m <sup>u</sup>
<i>Ic</i>	3.88	6.80 7.50	4.84 t (6.7)	3.00 d (6.7), 6.80 7.50 m
<i>IIc</i>	3.91	6.80 7.50	5.15 t (7.6)	3.49 and 3.51 (AB part of ABX system, 13.5, 7.6, 7.6) <sup>u</sup> , 6.80 7.5 m
<i>Id</i>	3.84	6.82 6.92	5.78 s	7.20 7.50 m
<i>IIId</i>	3.89	6.75 6.90	6.30 s	7.25 7.65 m
<i>Ie</i>		6.75 d and 7.23 d (9.0)	5.00 (X part of ABX system, 2.9, 9.5)	3.85 s, 3.95 and 4.10 (AB part of ABX system, 10.0, 2.9, 9.5) <sup>u</sup> , 6.8 7.0 m
<i>IIe</i>		6.81 d and 7.35 d (8.8)	5.29 t (7.2)	3.82 s, 4.51 and 4.55 (AB part of ABX system, 10.5, 7.2, 7.2) <sup>u</sup> , 6.85 7.00 m
<i>If</i>	3.90	6.70 7.10	4.84 d (2.9)	1.19 d (6.1) $\gamma$ -CH <sub>3</sub> , 3.88 s OCH <sub>3</sub> , 4.31 d q (6.1, 2.9) $\beta$ -CH, 6.70 7.10 m Ar
<i>IIIf</i>	3.90	6.75 7.05	5.09 d (6.0)	1.49 d (6.0) $\gamma$ -CH <sub>3</sub> , 3.86 s OCH <sub>3</sub> , 4.72 d q (6.0, 6.0) $\beta$ -CH, 6.75—7.05 m Ar
<i>V</i>	3.88	6.70 6.92	4.80 t (6.8)	0.96 t (7.2), 1.85 m <sup>u</sup>
<i>VI</i>	3.90	6.70 7.10	5.93 t (7.0)	1.05 t (7.5), 2.25 m <sup>u</sup>
<i>IX</i>	5.93	6.80 7.00	4.86 t (7.3)	0.96 t (7.3), 2.20 m <sup>u</sup>
<i>(E)-XI</i>	3.88	6.85 6.91	6.51 d d d (15.9, 1.5, 1.5)	4.28 d d (5.9, 1.5), 6.20 d t (15.9, 5.9)
<i>XII</i>	3.89	6.80 6.95	5.17 d d (6.2, 8.8)	2.54 and 2.74 m <sup>u</sup> , 3.46 m <sup>u</sup>
<i>(E)-XIII</i>	3.78	6.29 d (2.2), 7.43 d d (9.8, 2.2)		3.10 d t (6.3, 6.3) $\beta$ -CH <sub>2</sub> , 3.48 t
<i>(Z)-XIII</i>	3.82	6.25—6.55 m 6.48 d (2.2), 7.06 d d (9.8, 2.2)		(7.0) and 3.51 t (7.0) $\gamma$ -CH <sub>2</sub>

Table 1 (Continued)

Compound	OCH <sub>3</sub> (or OCH <sub>2</sub> O)	Ar (or QM)	$\alpha$ -CH	R
( <i>E</i> )- <i>XIV</i>	3.90	6.86—6.92	6.57 br d (16.0)	4.17 d (8.0), 6.23 d t (16.0, 8.0)
<i>XVI</i>	3.86	6.65—7.10	5.06 d (6.2)	0.98 t (7.1) $\gamma$ -CH <sub>3</sub> , 1.51 d (6.2) $\gamma$ -CH <sub>3</sub> , 2.17 m <sup>a</sup> $\beta$ '-CH <sub>2</sub> , 3.77 s OCH <sub>3</sub> , 4.73 d q (6.2, 6.2) $\beta$ -CH, 4.85 t (7.1) $\alpha$ '-CH, 6.65—7.10 m Ar
( <i>E</i> )- <i>XVII</i>	3.77	6.22 d (2.2), 7.44 d d (9.6, 2.2)	6.25—6.80 m	1.00 t (7.3) $\gamma$ -CH <sub>3</sub> , 1.65 d (6.7) $\gamma$ -CH <sub>3</sub>
( <i>Z</i> )- <i>XVII</i>		6.52 d (2.2), 7.02 d d (9.6, 2.2)		2.18 m <sup>a</sup> $\beta$ '-CH <sub>2</sub> , 3.87 s OCH <sub>3</sub> , 4.83 t (7.5) $\alpha$ '-CH, 5.35 d q (13.4, 6.7) $\beta$ -CH, 6.70—6.90 m Ar

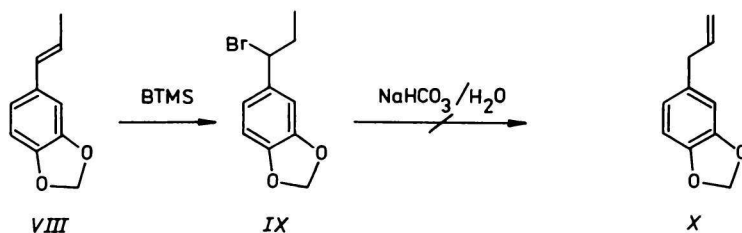
a) Diastereotopic methylene protons.

Table 2

<sup>13</sup>C NMR chemical shifts  $\delta$  of lignin model compounds

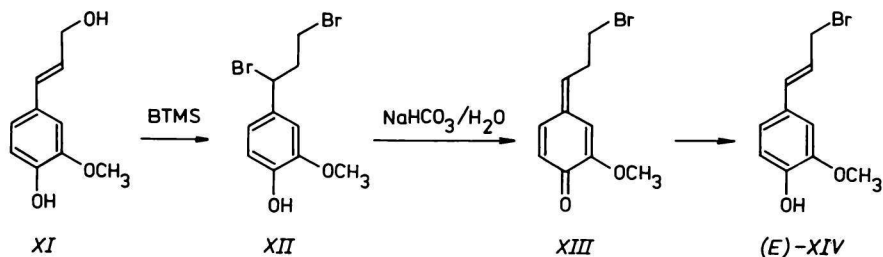
Compound	C- $\alpha$	C- $\beta$	C- $\gamma$	C-1	C-2	C-3	C-4	C-5	C-6
<i>Ib</i>	76.8	31.6	10.1	136.5	108.2	146.4	144.8	113.9	118.8
<i>IIb</i>	58.4	33.3	12.9	134.0	109.6	146.4	145.5	114.0	120.2
<i>VIIa</i>			—	120.0	110.6	146.4	145.5	114.4	121.2
<i>VIIb</i>				120.8	111.9	144.4	150.8	120.8	121.7
<i>XI</i>	131.1	125.8	63.5	129.0	108.2	146.5	145.3	114.3	120.0
<i>XII</i>	53.3	30.9	42.2	132.5	109.7	146.5	145.9	114.3	120.3

It has been found that in  $\text{CDCl}_3$  quinone methides *III* quantitatively and stereoselectively isomerize into corresponding (*E*)-*p*-hydroxystyrenes *IV* [4]. Therefore it was essential to see, if it is possible to regenerate quinone methides from these main products of their chemical transformation in neutral solution. We have demonstrated that BTMS reacts with *p*-hydroxystyrenes *IV* in a similar manner as with *p*-hydroxybenzyl alcohols *I*, so *p*-hydroxystyrenes seem to be appropriate starting compounds for syntheses of quinone methides *III*. Moreover, a treatment of  $\alpha$ -arylalkenes (but not  $\beta$ -arylalkenes) with BTMS yields bromides even when *p*-hydroxy group is protected. For example, isosafrole *VIII* gives bromide *IX* (Scheme 2) which is unsplitable with  $\text{NaHCO}_3/\text{H}_2\text{O}$ . Safrole *X* does not react with BTMS.



Scheme 2

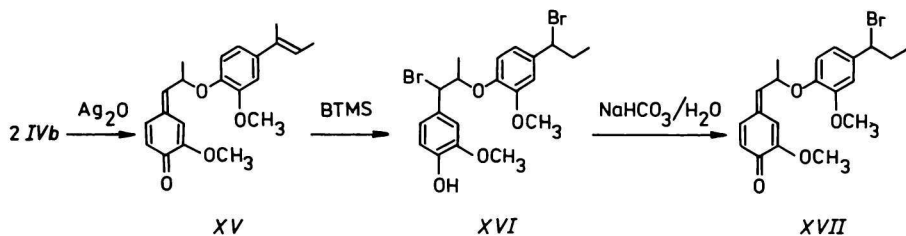
A combination of the reactions described gives us a way to obtain some interesting dibromides and brominated quinone methides, undoubtedly useful synthones in lignin chemistry. In this way, coniferyl alcohol *XI* gives dibromide *XII* and then bromide *XIII* (Scheme 3; compare the erroneous assignment [8]). Quinone methide *XV* [9, 10] gives dibromide *XVI* and then bromide *XVII* (Scheme 4). In both cases the presence of bromine atoms in  $\alpha$ -position is proved by characteristic positions of H- $\alpha$  and C- $\alpha$  signals in the NMR spectra (compare with other bromides; Tables 1 and 2). It is essential that the positions of the



Scheme 3

signals of  $\gamma\text{-CH}_2\text{Br}$  group of the compound *XIII* and that of  $\alpha'\text{-CHBr}$  proton of the aryloxy substituent of the compound *XVII* are practically the same as in the case of initial compounds *XII* and *XVI*, correspondingly. It means that a treatment with aqueous sodium hydrogen carbonate leaves these bromine-containing groups unchanged. The only doubt concerning the ascribing of structures might arise when we consider  $\gamma$ -position of the compound *XII*, because usually the reaction of BTMS with primary alcohols needs many hours at 50 °C [7]. Nevertheless, in the case of coniferyl alcohol *XI* bromination is a fast reaction at room temperature. The bromination of  $\gamma$ -position is proved by comparison of the positions of C- $\gamma$  atom signal in the  $^{13}\text{C}$  NMR spectrum with signals of  $\text{CH}_2\text{Br}$  of ethyl bromide ( $\delta = 27.6$ ) and  $\text{CH}_2\text{OH}$  of propanol ( $\delta = 64.1$ ); usually for primary alcohols  $\delta(\text{COH}) = 60\text{--}65$ , which is far from our experimental data (Table 2). The decisive evidence is the isomerization of quinone methide *XIII* into corresponding (*E*)-*p*-hydroxystyrene *XIV*: the  $^1\text{H}$  NMR spectrum of this compound corresponds to the ascribed structure and obviously differs from the spectrum of parent (*E*)-coniferyl alcohol *XI* (Table 1).

Our model experiments have demonstrated that BTMS (no matter whether itself or as a carrier of dry HBr) can transform alcoholic and unsaturated fragments of side chain of lignin polymer into bromine-containing subunits. Therefore a treatment of lignins with BTMS might be used as analytical



Scheme 4

Table 3

## The elemental analyses data

Samples	$w_i/\%$				$n_i^a$			
	C	H	O	Br	C	H	O	Br
1	55	5	23	17	9	7.9	2.1	0.5
2	57	5	25	13	9	7.5	2.3	0.3
3	54	5	22	19	9	8.1	2.1	0.5
4	55	5	23	17	9	7.9	2.1	0.5
5	56	5.5	28.5	10	9	8.8	2.8	0.3
6	53	5	28	15	9	8.3	2.9	0.4
MWL	62	6	32	—	9	8.6	2.9	—

a) This calculation of the number of atoms  $n_i$  per phenylpropane unit has been made for the methoxyl group content 0.9 per unit, taking into account the accuracy of bromine elemental analysis (1 %).

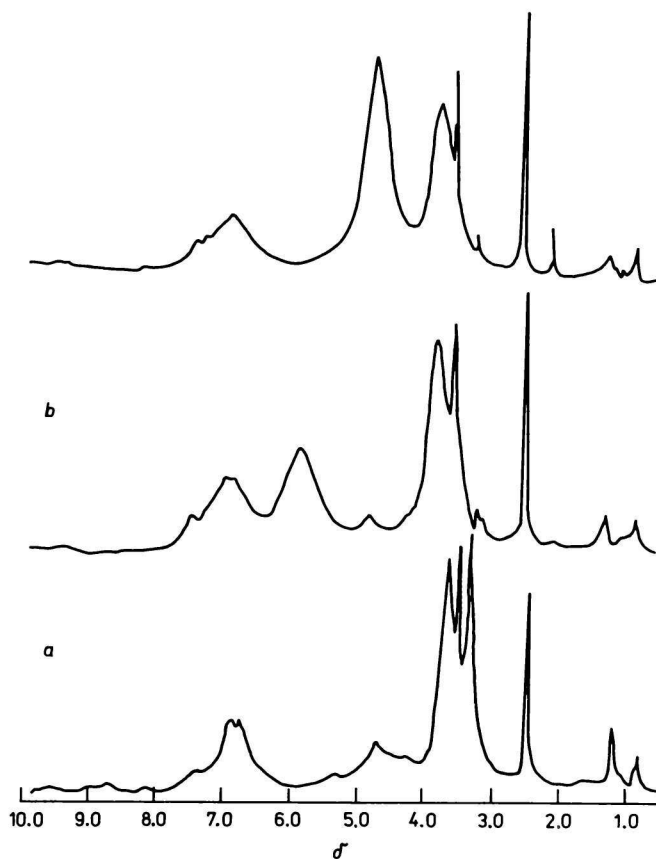


Fig. 1.  $^1\text{H}$  NMR spectra of lignin samples: MWL (a), brominated lignin 2 days after the synthesis (b), brominated lignin a month after the synthesis (c).



procedure as well as a way to transform lignins into their derivatives of higher chemical reactivity.

A treatment of black spruce MWL with BTMS in dioxane solution has led to its quantitative transformation into a product with high bromine content, but without silicon (Table 3; the silicon elemental microanalyses have also been done for all the samples, but these analyses have demonstrated an absence of silicon). The  $^1\text{H}$  NMR spectra (Fig. 1) demonstrate a sharp difference between the initial MWL and the product of bromination, but in high fields only. It is essential that in accordance with the data of elemental analyses there were no signals in the region of  $\delta = 0\text{--}1$  which might be ascribed to trimethylsilyl groups. The conclusion should be made that, as it is in the case of model compounds, BTMS itself brominates lignin, but without silylation. NMR data give a support to the idea that the procedure implemented affects side chains of lignin mostly, if not exclusively (compare the well known rough assignments of signals of different groups in lignin  $^1\text{H}$  NMR spectra [6]). It seems to be very improbable that BTMS or HBr can attack an aromatic ring in mild conditions: it is known that such nucleophilic reactants leave this ring unchanged; ring bromination takes place only when electrophilic reactants, for example, free bromine are used. But, accordingly to the synthetic procedure, there were no appreciable amounts of free bromine in BTMS. As an additional proof we regard a treatment of the sample of brominated with BTMS lignin by aqueous solution of 2 M-NaOH (8 h, boiling). This treatment obviously led to the elimination of bromine from a side chain, but not from an aromatic ring. The product contained less than 2 % of bromine, according to the data of elemental analysis. We suppose that the estimation obtained (one bromine atom per two phenylpropane units, see Table 3) corresponds approximately to the content of aliphatic hydroxy groups and double bonds in lignin (*cf.* [6, 11]). The brominated MWL decomposes slowly in the course of time, the content of bromine falls down (Table 3, sample 2) and the  $^1\text{H}$  NMR spectrum demonstrates qualitative changes in aliphatic region (Fig. 1).

A treatment of MWL with dry HBr itself has yielded a product of bromination, but with a bit smaller bromine content and with oxygen content intermediate between initial MWL and a product of its reaction with BTMS (Table 3, samples 5 and 6). It seems that in the conditions used HBr mostly adds to carbon—carbon double bonds, but it does not substitute  $\alpha$ -hydroxy groups.

*Acknowledgements.* This work was completed during the stay of the author at the Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Comenius University, Bratislava, in the framework of the Czechoslovak-Soviet cultural and scientific agreement. The authors wish to thank Professor J. Čižmárik and Dr. M. Remko for helpful discussions, Dr. O. V. Arapov for elemental microanalyses, and Dr. E. I. Evstigneev for a sample of the compound If.

## References

1. Ralph, J. and Young, R. A., *J. Wood Chem. Technol.* 3, 161 (1983).
2. Zakis, G. F., *Synthesis of Lignin Model Compounds* (in Russian). Zinatne, Riga, 1980.
3. Shevchenko, S. M., Yakobsons, Yu. K., Mishnev, A. F., and Liepinsh, M. G., *Zh. Strukt. Khim.* 30, 135 (1989).
4. Shevchenko, S. M., Apushkinsky, A. G., Gindin, V. A., and Zarubin, M. Ya., *Khimiya Drevesiny* (1990).
5. Shevchenko, S. M., Apushkinsky, A. G., Gindin, V. A., and Zarubin, M. Ya., *Zh. Org. Khim.* 26 (1990).
6. Grushnikov, O. P. and Elkin, V. V. *Progress and Problems of Lignin Chemistry* (in Russian). Nauka, Moscow, 1973.
7. Jung, M. E. and Hatfield, G. L., *Tetrahedron Lett.* 46, 4483 (1978).
8. Adler, E. and Stenemur, B., *Chem. Ber.* 89, 291 (1956).
9. Zanarotti, A., *J. Chem. Res. (M)* 1983, 2625. (*J. Chem. Res., Synop.* 12, 306 (1983)).
10. Shevchenko, S. M., Semenov, S. G., Evstigneev, E. I., Pranovich, A. V., and Gindin, V. A., *Zh. Org. Khim.* 23, 1891 (1987).
11. Adler, E., *Wood Sci. Technol.* 11, 169 (1977).