Theoretical study of environmental concern characteristics of different possible AOX compounds form lignin of paper mill effluent

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ABSTRACT

In the present paper an attempt was made to study the extent of AOX formation as secondary pollutants from the lignin of the paper mill effluent under existing conditions of chloride level, ammonia level, PH and temperature. It was found at PH of 6-8 and natural room temperature conditions there was a rise of AOX content up to 17% within 12 hours and 32% of increase after 24 h when chloride ion concentration 30 mg/L and ammonia was not present. Where as in presence of 15 mg/L of ammonia there was an increase up to 2% in 12 hours and 44% rise in 24 hours. The theoretically possible chloro- compounds from lignin building blocks were designed and their aqueous solubility at pH 7, log P, log D, adsorption coefficient and BCF values were obtained from computational methods using ACD lab soft ware and were compared to evaluate environmental concern possibilities.   © 2008 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Lignin produced during pulping process for papermaking is an environmental concern for the pulp and paper industry[1]. The lignin contained in fiber is converted into thio- and alkali-lignin during the Kraft pulping process and to lignosulfates in the sulfite pulping process for papermaking. Lignin is responsible for the colour of paper mill waste effluents. Discharge of coloured effluents from the pulp and paper mills is not only a serious aesthetic problem[2], but also interferes with algal and aquatic plant productivity by limiting light transmittance[3]. Environmental protection regulations are limiting the discharge of coloured waste effluents into receiving waters. Lignin is not decomposed by biodegradation through bacteria. Therefore they accumulate in nature and persist for a long time. Bleaching through HOCl is commonly adapted to remove the colour of or to sterilize water. But there is a chance of chlorination to lignin and to the hydrolysis products derived from lignin. These results the formation of the secondary pollutants like chlorinated organic molecules that are carcinogenic[4].

Chemicals

All chemicals of analytical grade chemicals and double distilled water were used.

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Experimental details and analytical methods

Stock solution of aqueous chlorine approximately 0.05M was prepared by bubbling chlorine gas into distilled water and stored at 5^0C temperature. The aqueous chlorine solution was standardized by iodine-thiosulfate titration using starch as indicator. Organic soluble lignin (OSL) was isolated through procedure followed by Tsuneo Kondo[5]. was taken in each of the three conical flasks of 1L capacity having 500 ml of distilled water. 1.7g of sodium chloride was added to 2nd and 3rd flasks. 4×10^{-4} moles of ammonia solution was added to 3rd flask. In this way four sets of each consists of three flasks were prepared. They labeled as 0, 6, 12, 24. All were allowed to stand undisturbed. After 6 hours of duration from the set labeled as 6 the lignin was isolated and subjected to AOX determination by pyrolysis-titrimetric method as specified in 21st Edition Standard Methods for the examination of water and waste water APHA, Wahington, D.C (2005)[6]. Similarly 12 and 24 labeled flasks werw too analyzed. Possible lignin building block structures were drawn through ACD lab soft ware and theoretical values of $pK_{a,}$ aqueous solubility, log p, log d and adsorption coefficient were obtained from soft were service provided by ACD lab.

RESULTS

The values of AOX after given in intervals is given TABLE 1. The bar graph of values are shown in figure 1.

TABLE 1: AOX value in μg/g of lignin

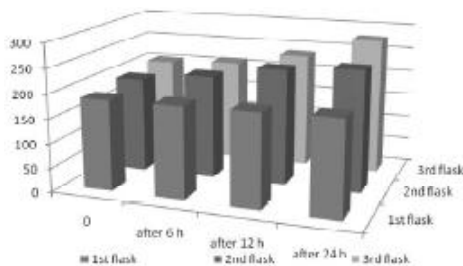| Sl.no	time	1st flask	2nd flask	2nd flask
1	0	186	195	195
2	After 6 h	187	212	212
3	After 12 h	189	237	237
4	After 24 h	192	269	269

Figure 1 : Bar graph of AOX values obtained for three different conditions i.e., in presence of residual chlorine, in presence of residual chlorine and chloride ion and in presence of residual chlorine, chloride ion, and ammonia

The possible structures are numbered from (**1 to 78**). The values log P, log D, Aqueous solubility at pH 7, adsorption coefficient and BCF obtained form software developed by Quantitative Structure Activity Relationship[7,8] Model software are given in TABLE 2.

DISCUSSION

There is practically negligible organic-chlorine content when aqueous chlorine alone was present with lignin. (Error 7%) In presence of chloride ion, after 6 h, there was a rise of 8% in AOX value. Similarly after 12 h and 24 h there was an increase of 21% and 27% in AOX value respectively. This observation supports

$$H^+ + Cl^- + HOCl \leftrightarrow Cl_2 + H_2O$$

Equilibrium was displaced far enough to right so that a significant reaction occurs between molecular chlorine and lignin. There may be a tendency to under go oxidative rupture of aromatic ring but in the present paper our discussion is limited to chloro-organic matter formation.

In presence of ammonia the increase in AOX was is found to be 4%, 16% and 36% respectively after 6h, 12h and 24h. When ammonia was present it reacts with chlorine faster than lignin to give NH_2Cl. It appears that NH_2Cl reacts with lignin more effectively than Chlorine. So there was an increase of 36% in AOX.

Bio concentration factor (BCF) is the concentration of a particular chemical in a tissue per concentration of chemical in water (reported as L/kg).

This physical property characterizes the accumulation of pollutants through chemical partitioning from the aqueous phase into an organic phase.

$$BCF= C_O/C_E$$

C_O is concentration of X in organism, C_E is Concentration of X in environment

A partition coefficient (P) or distribution coefficient (D) is the ratio of concentrations of a compound in the two phases of a mixture of two immiscible solvents at equilibrium[9]. Hence these coefficients are a measure of differential solubility of the compound between these two solvents. Hydrophobic drugs with high partition coefficients are preferentially distributed to hydrophobic compartments such as lipid bi-layers of cells while hydrophilic drugs (low partition coefficients) preferen-

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TABLE : 2 Computational generated log p, log d, solubility, adsorption coif and BCF

Structural unit	log P	log D	Solubility pH7	Adsorption Clef	BCF	Structural unit	log P	log D	Solubility pH7	Adsorption Clef	BCF
1	1.86	1.9	2.79	245	15.3	40	0.98	1	0.42	80.8	3.25
2	2.43	2.4	0.8	489	40.4	41	1.77	1.7	0.1	205	12.2
3	3.01	2.8	0.33	677	74.7	42	0.56	0.6	0.61	48.1	1.57
4	1.63	1.6	3.07	182	10.1	43	1.27	1.3	0.33	117	5.45
5	2.42	2.4	0.63	487	40.2	44	1.22	1.2	0.38	109	4.93
6	1.27	1.3	3.55	117	5.42	45	1.06	1.1	0.69	90.1	3.79
7	1.26	1.29	0.92	115	5.31	46	1.62	1.6	0.2	175	9.66
8	1.8	1.8	0.32	204	12.3	47	2.19	1.9	0.11	179	13.1
9	2.33	2.2	0.11	361	28.5	48	2.74	2.4	0.03	353	34.1
10	0.49	0.5	2.05	43.8	1.38	49	3.31	3	0.0084	708	90.9
11	2.42	2.4	0.14	489	40.3	50	3.33	3	0.014	723	93.7
12	3.1	3	0.043	990	115	51	0.65	0.6	0.75	53.7	1.83
13	3.49	3.4	0.018	1476	208	52	1.44	1.4	0.16	139	7.04
14	3.9	3.7	0.01	2062	354	53	0	0	1.2	23.7	1
15	1.18	1.2	0.085	105	4.68	54	4.36	4.4	0.00001	5571	1202
16	0.25	0.3	1.74	32.5	1	55	2.6	2.6	0.064	620	56
17	0.82	0.8	3.29	66.1	2.45	56	2.89	3	0.03	784	64
18	2.02	2	0.23	297	20	57	2.71	2.7	0.033	704	66.8
19	2.57	2.6	0.077	568	50.5	58	3.2	3.19	0.023	846	89
20	3.14	2.8	0.055	501	59.1	59	3.5	3.5	0.002	952	103
21	3.7	3.33	0.016	931	145	60	4.2	4.19	0.0006	1026	127
22	1.6	1.6	0.27	177	970	61	1.18	1.1	0.072	156	10
23	2.39	2.4	0.066	454	36.8	62	2.2	2.18	0.03	163	15
24	2.29	2.3	0.16	416	32.1	63	2.4	2.39	0.002	169	25
25	2.84	2.8	0.073	804	81.8	64	2.6	2.56	0.0001	172	37
26	3.4	3.4	0.023	1612	216	65	3.1	2.99	0.00001	183	46
27	3.3	3.3	0.038	1463	187	66	3.1	3.11	0.000001	199	59
28	4.54	4.5	0.0073	1960	463	67	3.5	3.48	1E-07	206	73
29	1.7	1.7	0.33	199	11.4	68	1.84	1.8	0.049	239	14.8
30	2.49	2.5	0.079	514	43.7	69	2.2	2	0.0033	258	26
31	3.27	3.3	0.018	1377	173	70	2.4	2.37	0.0002	345	56
32	3.5	3.47	0.012	1425	189	71	0.87	0.9	0.0036	91	2.3
33	4.24	4.2	0.002	1634	218	72	2.8	2.7	0.000019	456	69
34	4.34	4.3	0.0006	1689	223	73	3.4	3.37	0.00001	568	86
35	0.87	0.9	0.67	70.3	2.67	74	3.8	3.77	0.00001	679	105
36	1.5	1.5	0.31	158	8.26	75	4.2	4.19	0.000001	906	214
37	2.07	2	0.1	299	20.7	76	1.63	1.6	0.051	184	10.3
38	2.64	2.2	0.084	234	21.5	77	1.9	1.89	0.006	199	19
39	3.42	2.9	0.018	579	78.5	78	2.2	2.19	0.003	229	26

tially are found in hydrophilic compartments such as blood serum.

Normally one of the solvents chosen is water while the second is hydrophobic such as octanol. The partition coefficient is a ratio of concentrations of un-ionized compound between the two solutions[10].

**Log P oct/wat =log({solute}octanol/[solute] un ionized water)**

The logarithm of the ratio of the sum of concentrations of the solute's various forms in one solvent, to the sum of the concentrations of its forms in the other solvent is called log D.

**Log D= log[solute] octanol/[solute]ionized water+[solute] neutral water**

The hydrophobicity of a compound can give scientists an indication of how easily a compound might be taken up in groundwater to pollute waterways, and its toxicity to animals and aquatic life[11]. Log P, log D, absorption coefficient and BCF decreases by methoxyl groups.

Aqueous solubility is increased by methoxyl group substitutions. In chlorine substitution molecule the log P, log D, absorption coefficient and BCF increases and aqueous solubility decreases on increasing no of chlo-

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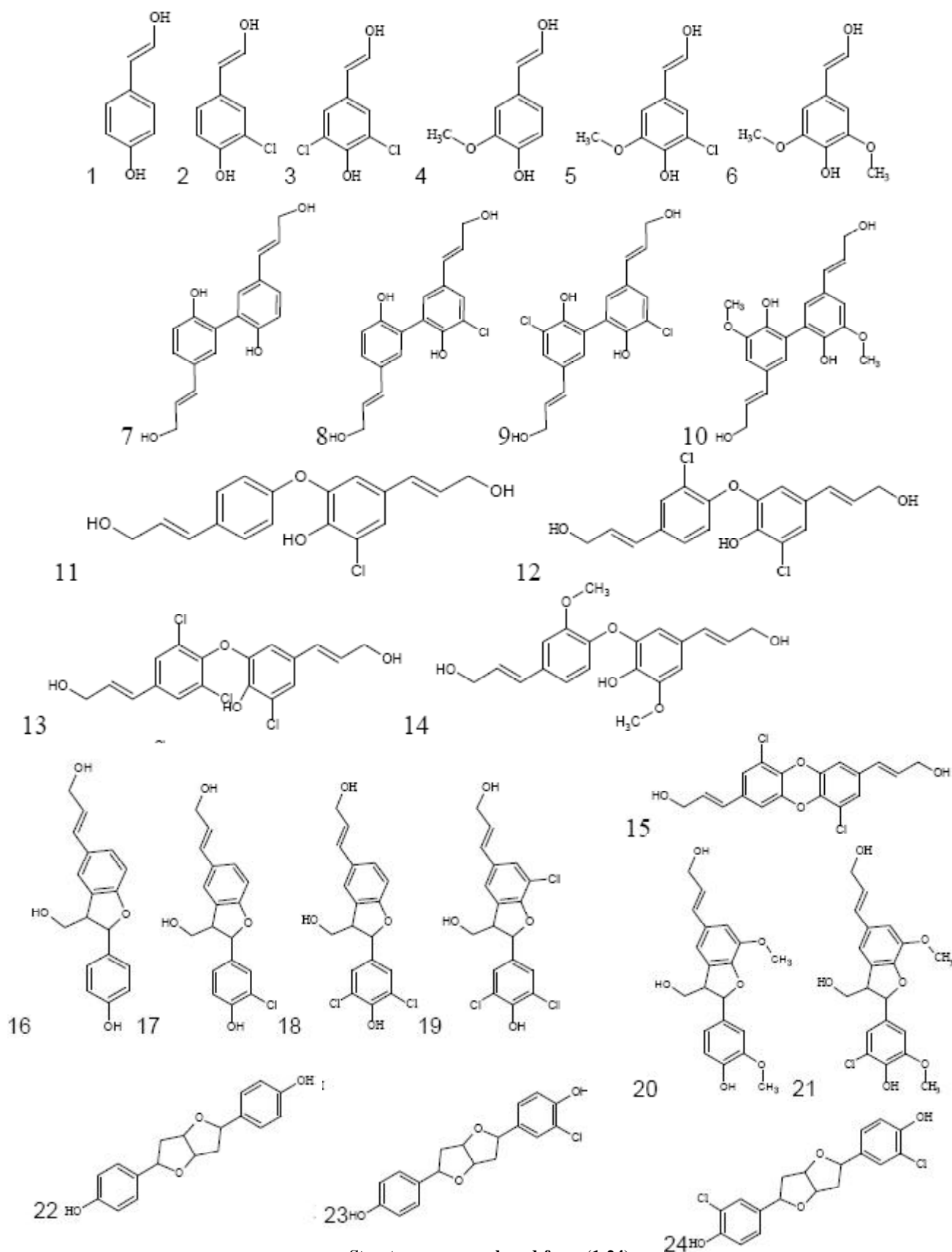
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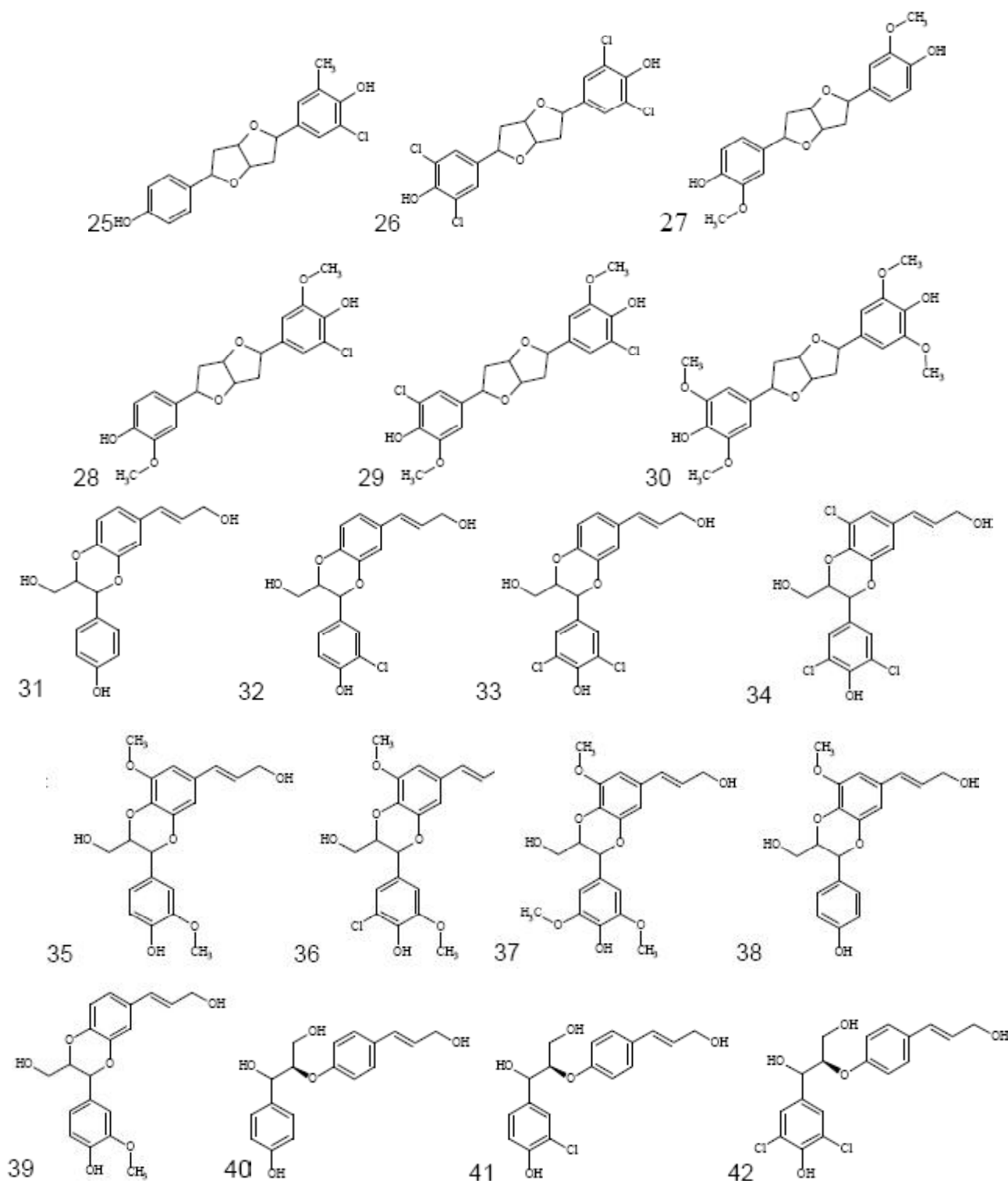
Structures are numbered from (25-42)

rine atoms. On comparing the value attributed to differ-
ent dimers and trimer formed by different possible link-
ages, The resinol **(22)** is formed through β-β or α-O-
γ' linkage is found to be having the highest BCF i.e.,

970. Arylisochroman **(57)**, dibenzodioxocin **(49)** are
formed by 5-5/β-O-4(α-O-4) linkage and
benzodioxane **(31)** is formed by β-O-4(α-O-5)link is
found to have significant BCF values. Benzdioxane **(61)**

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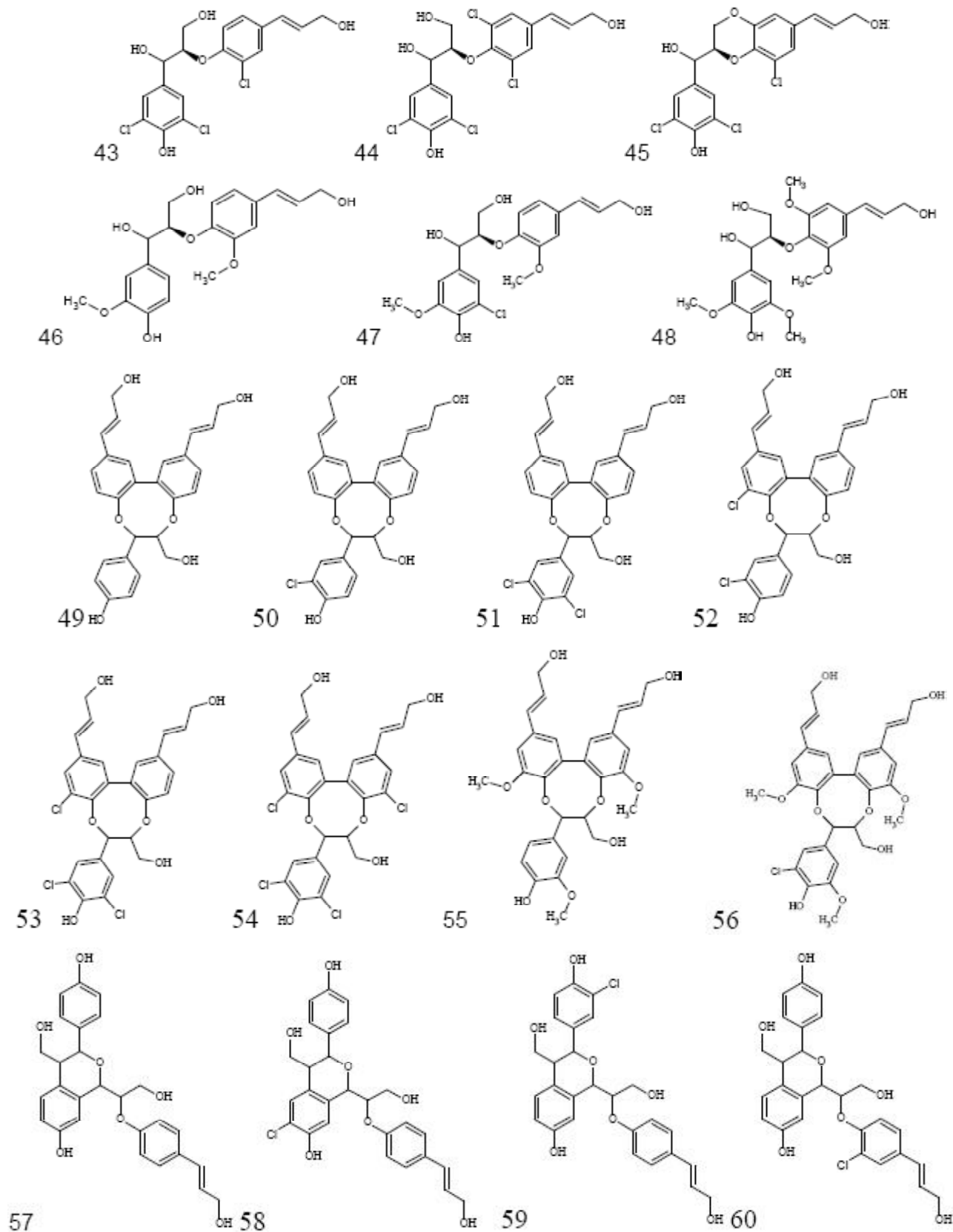
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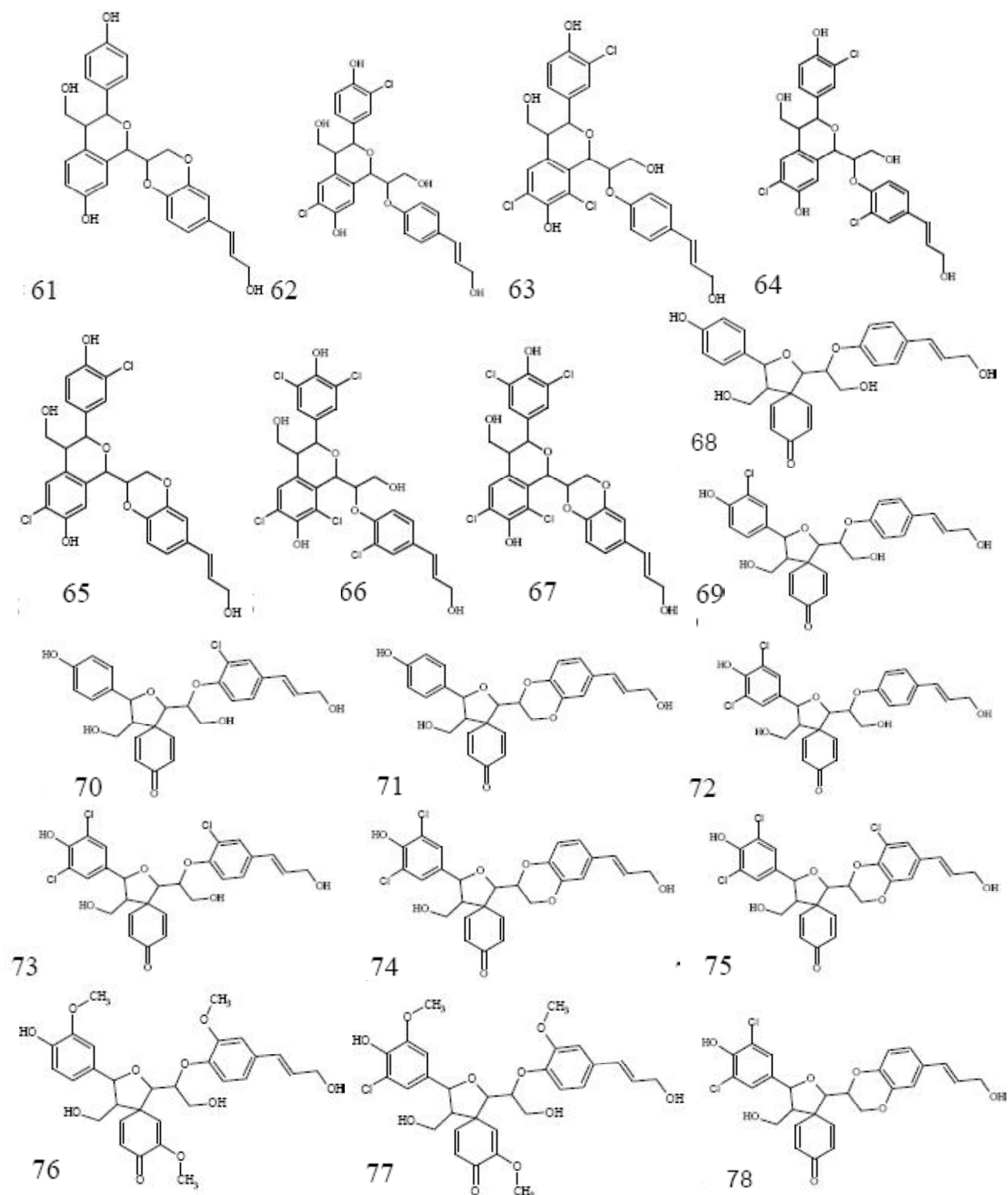
Structures are numbered from (61-78)

and spirodienone **(68)** have less significant BCF. The structures **(7)**, **(15)**, **(40)**, and **(71)** have little BCF. phenylcoumaran **(16)** is formed through β-5 (α-O-4) link has BCF value 1. Aqueous solubility is found to be decreasing from monomer to dimer and to trimer. Among dimers phenyl-coumaran is found to has high aqueous solubility. So though it has very less BCF the solubility factor plays role in bio accumulation. Though

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BCF value has a strong correlation with log P and adsorption coefficient values the dibenzodioxocin has more log p/adsorption coefficient values but posses less BCF value than benzodioxane. It is observed that there will be drastic change in properties whenever structural change caused due to ring closing occurs through elimination of HCl (13→15, 60→61, 64→65, 66→67, 70→71 and 73→74). All such changes are characterized by increase in solubility and decrease in other considered parameters.

High potential BCF>1000; moderate potential 1000 >BCF>250; low potential 250>BCF on this criteria 22 and 54(border line case) have high potential 14 and 28 have moderate potential and remaining are low potential molecules to enter into food chain of ecosystem..

For un-ionizable compounds, log P = log D for most of the case this condition is observed.

CONCLUSIONS

The lignin material reacts with residual chlorine to generate secondary pollutants.

There are different chloro substituted derivatives depend up structure aspects. On their physiological and environmental characteristics they may get enter into food chain. Log P, log D, absorption coefficient and BCF decreases by methoxyl groups. Aqueous solubility increases by methoxyl groups. In chlorine substitution molecule the log P, log D, absorption coefficient and BCF increases and aqueous solubility decreases on increasing no of chlorine atoms. There will be drastic change in properties whenever structural change caused due to ring closing occurs through elimination of HCl.

ACKNOWLEDGMENT

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