ADSORPTION PROPERTIES OF LIGNINS RELATIVE TO THE COMPONENTS OF PLANT OIL

M. R. Yakubova, L. S. Smirnova, D. T. Asilbekova,
S. D. Gusakova, B. Kh. Pulatov, Kh. A. Abduazimov,
and A. I. Glushenkova

UDC 547.992.00:61+665.329

A comparative investigation has been made of the sorption properties of three unmodified and nine modified hydrolysis lignins in relation to the lipophilic and lipid components of plant oils.

We have previously studied the sorption properties of adsorbents based on hydrolysis lignins (HLs) in the process of decolorizing and purifying aqueous solutions from pigments and high-molecular-mass substances [1] and from bacterial cells and their toxins and cholesterol [2]. The behavior of HLs and modified adsorbents obtained from them (MHLs) on contact with hydrophobic lipid mixtures of plant nature has not previously been studied.

We have investigated the sorption properties of unmodified HLs and MHLs in relation to "crude" apricot-kernel, peach-kernel, grape-seed, pomegranate-seed, and cottonseed oils. The crude kernel and seed oils obtained from the wastes of the preserving and winemaking industries have not found wide use in the food and pharmaceutical sectors because of the presence of undesirable impurities and pigments in them.

Cottonseed oil is one of the dark-colored oils difficult to refine, the alkaline raffination of which is accompanied by considerable losses.

As the unmodified products we used HLs from rice husks, from a conifer, and from cottonseed hulls. MHLs were obtained from the cottonseed hull HL: they were nitrosulfo-, sulfo-, nitro-, chloro-, demethylated, oxidized, piperidinomethylated, phosphorylatedpiperidinomethylated [3], and ammonized [4] lignins.

All the HLs were first washed with water and treated with organic solvents, since the water washing of technical HLs extracts the last traces of sulfuric acid, reducing substances, and monohydric phenols [5], while organic solvents [6] eliminate lignocarbohydrates and resinous substances [7].

A solution of an oil in a nonpolar organic solvent was brought into contact with the HLs and MHLs at various ratios of the weights of the lignin and of the oil until a clear solution of the latter had been obtained, and this was separated from the lignin by filtration through a paper filter. The lignin was washed several times with the same solvent, the completeness of desorption of the lipid components being monitored by the TLC method (system 1).

Our results show that the clarification of apricot-kernel, peach-kernel, and grape-seed oils by all the lignins investigated except the nitrosulfolignin took place at the same ratio (g/g) of lignin to oil, of 2:1. The clarification of these oils on nitrosulfolignin required a lignin to oil ratio of 3:1, while for pomegranate-seed and cottonseed oils this magnitude ranged between 3 and 6. Somewhat better sorption properties of modified HLs were expressed in the clarification of cottonseed oil for which an MHL to oil ratio of 4:1 was sufficient against one of 5-6:1 for the unmodified HLs. This positive effect did not depend on the method of modifying the HLs. Consequently, the adsorption properties of MHLs did not depend on the nature of the polar functional groups introduced into the lignin molecule.

The pomegranate-seed and cottonseed oils, unlike the kernel oils, were clarified less well by the oxidized HL in spite of the fact that this HL had the highest value of the maximum adsorption of all the MHLs. All the oils except cottonseed oil were clarified better

---

Institute of the Chemistry of Plant Substances, Uzbekistan Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, Nos. 3,4, pp. 323-327, May-August, 1992. Original article submitted October 17, 1991.

TABLE 1. Characteristics of the Crude Oils and Those Clarified by Piperidinomethylated Lignin

Oil	Yield, % on the weight of the sample		Acid No., mg KOH		Color*	
	clarified	polar component, pigments	crude	clarified	crude	clarified
Apricot-kernel	93,5	6,5	5,73	1,86	24	5
Peach-kernel	94,0	6,0	5,89	3,51	Не просм.	10
Grape-seed	90,0	10,0	4,75	1,49	Не просм.	3,0
Cottonseed	89,0	11,0	5,68	4,62	Не просм.	10
Permanga	88,0	12,0	7,70	1,94	44	12

---

*In red units at 35 yellow units in a 13.5-cm layer.

TABLE 2. Fatty Acid Compositions of the Crude Oils and Those Clarified by Piperidinomethylated Lignin

Oil	Fatty acids, % by GLC									
	12:0	14:0	16:0	17:0	18:0	18:1	18:2	18:3	18:3 con.	20:0
Apricot-kernel										
crude	—	Tr.	2,8	Tr.	Tr.	71,5	25,7	—	—	Tr.
clarified	—	Tr.	4,0	Tr.	1,0	69,7	25,3	—	—	Tr.
Peach-kernel										
crude	—	1,0	5 0	0,8	Tr.	72,8	20,4	—	—	—
clarified	—	1,0	5,2	0,4	Tr.	74,2	19,2	—	—	—
Grape seed										
crude	—	0,7	4,7	—	2,4	18,3	72,0	1,9	—	—
clarified	—	0,8	6,8	—	2,5	22,6	67,3	Tr.	—	—
Cottonseed										
crude	Tr.	0,5	20,8	Tr.	1,7	18,2	58,8	Tr.	—	Tr.
clarified	Tr.	0,5	24,8	Tr.	2,1	17,8	54,8	Tr.	—	Tr.
Permanganate-seed										
crude	0,5	0,3	5,6	0,6	2.7	15,3	17,9	—	56,7	0,4
clarified	0,4	0,2	5,9	3,4	2,2	16,1	14,4	—	56,5	0,9

by such MHLs as demethylated and phosphorylated piperidinomethylated lignins, which had small but close values of the maximum adsorption [3]. The adsorption properties of the other five MHLs in relation to the components of the plant oils investigated were comparable with one another.

It follows from what has been said above that the sorption of the pigmentary components of the crude plant oil by lignins is determined to a large degree by the nature of the lipophilic pigments. It is known that crude cottonseed oil contains polyphenolic pigments of gossypol nature [8]. The color of grape seed oil is due to a complex of native and modified forms of chlorophyll pigments [9]. There is no information in the literature on the pigmentary complexes of crude apricot-kernel, peach-kernel, and pomegranate-seed oils. The polar lipids of the plant oils were phospho- and glycolipids.

On using the piperidinomethylated HL (PMHL) we determined gravimetrically the yields of purified oils for all the samples (fraction 1). The pigments and other components of the oils adsorbed on the PMHL (fraction 2) were extracted from the sorbent with polar solvents, after the evaporation of which their yields were determined and their compositions were analyzed by TLC in system 2. Compounds of known structure were used for the identification of the lipids.

The crude and purified oils were analyzed similarly and were characterized with respect to color, acid No., and fatty acid composition by the GLC method, the results being given in Tables 1 and 2.

According to TLC, all the oils studied contained triacylglycerols (R_f 0.80, system 1), free fatty acids (R_f 0.52), oxidized and incomplete acylglycerols, phytosterols (R_f 0.40-0.44), more polar lipid and lipophilic components (R_f 0.40-0.10), and pigments (start), the color of which varied from yellow to dark brown or, in the case of the grape-seed oil, from greenish-brown to brown.

The purified oils contained, in addition to triacylglycerols, very small amounts of free fatty acids and pigments (TLC, Table 1), and traces of the other lipids mentioned above.

For all the oils except the pomegranate-seed oil, the components feebly sorbed on PMHL (fraction 2) consisted mainly of pigments, polar lipids, and lipophilic components, with traces of triacylglycerols and FFAs. The yields of these components ranged between 6 and 12% (Table 1), depending on the nature of the oil.

The oils studied differed with respect to their fatty acid compositions (Table 2). The apricot-kernel and peach-kernel oils were enriched with oleic (18:1) acid, and the grape-seed and cottonseed oils with linoleic (18:2), which has nonconjugated double bonds, and the pomegranate-seed oil with punicic (18:3) acid, which has three conjugated double bonds in the cis, trans, cis-configuration and is capable of undergoing rapid oxidation and polymerization [10].

A comparison of the fatty acid compositions of the crude oils and those contacted with the PMHLs showed that no appreciable changes in this index had taken place for the purified apricot and peach oils. In the case of the grape-seed, pomegranate-seed, and cottonseed oils, instantaneous decrease in the yield of purified oil (Table 2) was accompanied by a fall in the amount of the 18:2 acid and a parallel increase in the proportion of certain saturated acids and the 18:1 acid. It must be mentioned that the amount of punicic acid in the pomegranate oil had not changed after its contact with the PMHL.

The fall in the level of the 18:2 acid in the purified oils can be explained by the stronger adsorption on the lignin of triacylglycerols enriched with the 18:2 acid or by the influence of the level of lipophilic pigments on the sorption of such lipids.

By making use of the methods of IR spectroscopy (ν_{max}^{film} 1110, 1185, 1230, 1735, 3470 cm^{-1}) and of UV spectrophotometry ($\lambda_{max}^{cyclohexane}$ 240, 275, 285 nm) it was established that the components responsible for the color of the crude pomegranate-seed oil (in fraction 2) were represented by products of the polymerization of triacylglycerols enriched with punicic acid [10].

Thus, all the lignins investigated were capable of weakly retaining triacylglycerols having polyenic fatty acids with nonconjugated double bonds, of more strongly retaining free fatty acids, and of most strongly retaining polar lipids and lipophilic compounds, including pigmentary substances.

The properties of hydrolysis lignin as an adsorbent in relation to the clarification of plant oils are comparable with those of silica gel, since on both sorbents the strength of sorption of the lipids increases with a rise in their relative polarity.

The manifestation of sorption properties by HL can be explained by a combination of its properties. In the process of obtaining HL from lignocellulose, the cellulose is cleaved and eliminated in the form of monosaccharides in the aqueous phase. During this process the partial cleavage and condensation of lignin monomers and the subunits of the HL take place with a new spatial structure (lattice) possessing new functional groups — phenol, methoxy, carboxy, and carbonyl groups [11].

Technical HL is a three-dimensional highly aggregated high-molecular-mass polymer. The spatial lattice of HL apparently possesses molecular-sieve properties. The aromatic and aliphatic hydroxy, carboxy, and methoxy groups of HL are capable of forming hydrogen bonds with the molecules of the sorbate in a similar way to the silane groups of silica gel.

A specific property of lignin is its interaction with atmospheric oxygen, leading to the accumulation of free-radical forms of oxygen and of phenols in the lignin [12]. In their turn, phenolic pigments such as gossypol dissolved in a plant oil [8], and also unsaturated fatty acids [13], react similarly with O_2 to form free radicals. The reactions of the free radicals of the lignin and of the sorbate molecules with the appearance of unstable charge-transfer complexes [14] may be considered as one more form of sorption interaction.

EXPERIMENTAL

IR spectra were taken on a UR-20 instrument in a film, and UV spectra on an SF-26 spectrophotometer in cyclohexane.

GLC was conducted on a Chrom-4 instrument with a flame-ionization detector. A steel column with dimensions of 4 × 2500 mm filled with Chromaton N-AW-DMCS containing 17% of ethylene succinate was used. The fatty acid methyl esters were analyzed at 196°C.

TLC was conducted on Silufol (Czechoslovakia) in system 1 (hexane—diethyl ether—CH_3OOH (70:30:1) for the neutral lipids and in system 2 (chloroform—methanol—25% ammonia) for the phospho- and glycolipids. The plates were visualized with I_2 vapors or with 50% H_2SO_4 followed by heating.

The crude oils from the stone and seed fruits were obtained from the Kokand oils and fats combine, and the cottonseed oil from the Tashkent oils and fats combine. The methods of obtaining the MHLs are described in [3, 4].

Acid numbers and colors of the oils were determined by the methods described in [15]. To determine its fatty-acid composition, an oil was saponified with 10% KOH in MeOH at room temperature. The fatty acids isolated were methylated with CH_2N_2 and the methyl esters were analyzed by GLC. Each oil was clarified in a flask by the addition of the sorbent to a 10-15% solution of the oil in a hydrocarbon solvent.

LITERATURE CITED

1. V. A. Ryk and E. I. Akhmina, 7th All-Union Conference on the Chemistry and Utilization of Lignin: Abstracts of Lectures [in Russian], Riga (1987), p. 224.
2. V. P. Levanova, N. A. Belyakov, É. Kh. Pulatov, V. M. Demchenko, A. V. Solomennikov, A. I. Shugaev, T. A. Boiko, and I. S. Artem'eva, 7th All-Union Conference on the Chemistry and Utilization of Lignin: Abstracts of Lectures [in Russian], Riga (1987), p. 237.
3. L. S. Smirnova, M. R. Yakubova, B. Kh. Pulatov, and Kh. A. Abduazimov, Khim. Prir. Soedin., 414 (1991).
4. Z. K. Saipov, M. Khamidov, and Kh. A. Abduazimov, 6th All-Union Conference on the Chemistry and Utilization of Lignin: Abstracts of Lectures [in Russian], Riga (1976), p. 203.
5. V. G. Kostenko, V. A. Rumyantseva, I. I. Korol'kov, and E. L. Sarkisova, Gidroliz. Lesokhim. Prom-st, No. 1, 16 (1984).
6. V. G. Gorokhova, L. N. Petrushenko, G. P. Vasyanovich, N. Serdobol'skii, V. A. Babkin, A. V. Isaeva, and V. P. Levanova, Gidroliz. Lesokhim. Prom-st, No. 8, 9 (1987).
7. V. I. Ivanov, A. A. Chuksanova, and L. I. Sergeeva, Izv. Akad. Nauk SSSR Ser. Khim., 503 (1957).
8. S. D. Gusakova, D. T. Asilbekova, I. P. Nazarova, T. V. Khomova, A. A. Tyshchenko, and A. I. Glushenkova, Khim. Prir. Soedin., 42 (1988).
9. Yu. L. Zherebin and A. A. Kolesnik, Khim. Prir. Soedin., 663 (1983).
10. L. N. Koley, Fette, Seifen, Anstrichmittel, No. 8, 464 (1972).
11. M. I. Chudakov, The Industrial Use of Lignin [in Russian], Moscow (1972), p. 120.
12. É. I. Chupka and T. M. Rykova, Khim. Prir. Soedin., No. 2, 269 (1987); É. I. Chupka and V. V. Vershal', Khim. Prir. Soedin., No. 1, 121 (1986).
13. J. M. Campbell, R. B. Caton, and D. N. Crozier, Lipids, No. 11, 916 (1974).
14. Z. V. Todes, Ion-Radicals in Organic Synthesis [in Russian], Khimiya, Moscow (1986).
15. Handbook on Methods of Investigation, Technical and Chemical Control, and the Accounting of Production in the Oils and Fats Industry [in Russian], Leningrad, Vol. 1 (1965).