HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF ALKALOIDS

B. D. Kabulov, A. L. D'yakonov,
and S. V. Zalyalieva

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Literature information on the HPLC of alkaloids, including adsorption, reversed-phase, ion-exchange, ion-pair, and other variants is generalized. Results are given of the chromatographic analysis of various classes of alkaloids with an indication of the conditions of separation, and the columns used, and also of the methods of detection. The advantages and disadvantages of the HPLC variants are discussed. The review includes the literature over the last 14 years.

Numerous investigations have shown that high-performance liquid chromatography (HPLC) is one of the most important methods of separating such complex mixtures as plant extracts. The high efficiency of this method and the broad possibilities of the selection of suitable conditions of analysis (sorbent, eluent, method of detection) permit the separation and isolation of chemically and thermally unstable compounds, and also compounds with close properties and numerous isomers present as constituents of plants.

At the present time, a large number of studies devoted to the use of HPLC for separating natural compounds, including alkaloids, present in the plants of many families, have been published. These publications are scattered over a large number of journals. In view of which certain difficulties arise in finding suitable conditions of analysis for any concrete case of chromatographic separation. Furthermore, alkaloids are an extremely broad class of compounds subdivided into a number of groups with structures differing from one another. Information on the HPLC of these compounds has been most widely generalized in reviews [1-4] and a monograph [5] in which the adsorption, partition (liquid–liquid), and ion-exchange variants of liquid chromatography have been discussed.

In recent years, thanks to the use of octadecylsilylated silica gel sorbents, the HPLC of alkaloids has been considerably improved, which has provided new possibilities for qualitative and quantitative analysis, particularly in the field of investigation of the biosynthesis and metabolism of alkaloids. In this paper, the use of HPLC variants in the analysis of various alkaloids is generalized with a discussion of questions connected with methods of detection and the use of stationary and mobile phases.

DETECTION IN THE HPLC OF ALKALOIDS

UV and fluorimetric detectors are used most frequently in the HPLC of alkaloids, while electrochemical and refractometric methods are used more rarely.

Because of absorption in the UV region, a UV detector with a variable wavelength is the main apparatus for the detection of alkaloids in HPLC. It consists of a general-purpose spectrophotometer (absorbing in the UV or visible region with manual micrometric tuning of the monochromator. In use, a wavelength is selected at which all the components of interest in the sample absorb. During the elution of a sample in quantitative analysis it is undesirable to change the wavelength setting.

In recent years, UV detectors permitting the performance of a rapid automatic change in wavelength in 1-2 sec in the range of wavelengths from 190 to 600 nm have been developed. This makes possible the time-programming of a number of wavelength changes performed during the chromatographic analysis of a complex mixture.

The senstivity of the UV method of detection depends on the $E_{1\,cm}^{1\%}$ value of the alkaloid at the detection wavelength (usually 254 or 380 mm), and therefore equal areas of the

Scientific Center for Chromatography, Institute of Chemistry and Physics of Polymers, Uzbek Academy of Sciences, Tashkent. Institute of the Chemistry of Plant Substances, Uzbek Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 595-613, September-October, 1991. Original article submitted November 5, 1990.

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TABLE 1. Stationary Phases Used for the HPLC of Alkaloids

Phase	S_{sp}, m^2/g	v_p, cm^3/g	d_p, nm	Manufacturer
Nucleosil SI-60	500	0,7—1,0	6	M-N 6
Microsorb	300	"	10	
Hypersil	170	0,6—0,7	10,30	Shandon Southern
Nucleosil C_8	300	"	10	M-N 6
Nucleosil C_{18}	300	"	10	
Partisil-ODS	400	"	5	Whatman 2
μ-Bondapak C_{18}	300	"	10	Waters 13
μ-Bondapak Ph	300	"	10	
LiChrosorb RP-8	300	"	10	Merck 7
LiChrosorb RP-18	300	"	10	
Zorbax ODS	350	"	7	Du Pont 3
Spherisorb ODS	220	"	8	P.S. 14
μ-Bondapak CN	300	"	—	Waters 13
Spherisorb CN	220	"	8	P.S. 14
Nucleosil CN	300	"	10	M—N 6
Zorbax CN	350	"	7	Du pont 3
μ-Bondapak NH_2	300	"	—	Waters 13
Nucleosil NH_2	300	"	10	M-N 6
Zorbax NH_2	350	"	7	Du Pont 3
LiChrosorb NH_2	330	"	10	Merck 7

*Abbreviations. P.S.) Phase Separations; M—N) Macherey—Nagel.

peaks on the chromatogram of a mixture of different alkaloids do not mean that equal amounts of the alkaloids are present in the sample. A deficiency of UV detection is that it is possible to use only nonabsorbing solvents as the mobile phases.

Fluorimetric detection is more selective and sensitive. A fluorimeter depends to a smaller extent than other detectors on changes in the temperature or the pressure, but it is sensitive to impurities in the mobile phase (for example, dissolved oxygen) which are capable of causing a quenching of the fluorescence.

STATIONARY PHASE

In modern HPLC the main stationary phase used consists of silica gel with particle dimensions of from 5 to 10 μm. These sorbents are of medium porosity, the average pore diameter being 5-10 nm (Table 1).

It is known that porous particles with a grain size of 5 μm give the smallest HETP values and have a fairly high capacity (0.5 mg/g of adsorbent) [1]. Filling columns with such sorbents requires a special technique.

The choice of stationary phase for the analysis of alkaloids method depends on the problem to be solved and the nature of the alkaloids.

ADSORPTION HPLC OF ALKALOIDS

Alkaloids are substances with extremely high capacity for being adsorbed. This is due to the presence of a free pair of electrons at a nitrogen atom, thanks to which interaction takes place with the acid centers of the adsorbents. Because of the strong affinity for the adsorbents, a sharp separation of the alkaloids by the adsorption method is difficult, and therefore a careful choice of the conditions of separation is necessary for successful analysis.

Table 2 gives the conditions for the adsorption HPLC of various groups of alkaloids. As the stationary phases are widely used such adsorbents based on silica as Nucleosil [6], Hypersil [7], LiChrosorb SI-60 [8, 10, 16, 20-22, 25, 26, 28, 29, 33a], μ-Porasil [13, 12, 30, 32], Spherisorb [18, 19a, 27], MicroPak [23, 29], and Zorbax [31]. The mobile phases consist of mixtures of solvents with different polarities. To improve separation and to raise eluent power, alcohol [25, 27, 29, 30], ammonia [6, 11, 12, 17-19a, 33a), diethylamine [7-9, 14-16, 23, 24, 32], or triethylamine [13, 28, 33b] is added. In the separation of the majority of alkaloids the pH of the mobile phase must be above 7, since under these conditions ionization is suppressed and the chromatographed peaks contract. At the same time, at high pH values dissolution of the silica gel is observed. For this reason prefer-

TABLE 2. The Adsorption HPLC of Alkaloids

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Pyridine Alkaloids				
Nicotine, cotinine	Nucleosil	Dichloromethane—diisopropyl ether—methanol—NH_4OH (62:30:7.9:0.1)	UV (260 nm)	6
Quinoline Alkaloids				
Quinidine, quinidinone, cinchonine, hydroquinidine, cinchonidine, quinine, hydrocinchonidine, hydroquinine	Hypersil	n-Hexane—dichloromethane—methanol—diethylamine (66:31:2.6:0.5)	UV (312 nm)	7
Quinidinone, epiquinidine, epiquinine quinidine, cinchonine, cinchonidine, quinine, hydroquinidine, hydroquinine	LiChrosorb Si 60	Chloroform—isopropanol—diethylamine—water (940:57:1:2.65)	"	8
Cinchonine and others	"	Toluene—ethyl acetate—diethylamine (7:2:1)	UV (325 nm)	9
Quinidine, quinine, cinchonine, dihydroquinine, dihydroquinidine, cinchophylline	"	Chloroform—methanol—NH_4OH (500:7:1)	UV (280 nm)	10
Cinchonine, cinchonidine, quinidine, quinine, and others	Altex Ultrasphere-Si	THF—n-butyl chloride—NH_4OH (60:40:0.65)	UV (254 nm)	11
Isoquinoline Alkaloids				
Codeine	μ-Porasil	Dichloromethane—methanol—NH_4OH (90:10:0.1)	"	12
Moscapine, papaverine, thebaine, caffeine, morphine	μ-Porasil	n-Hexane—dichloromethane—ethanol—triethylamine (300:60:60:20)	UV (280 nm)	13
Narcotine, papaverine, thebaine, caffeine, morphine	"	n-Hexane—dichloromethane—ethanol—diethylamine (300:30:40:0.5)	"	14
Emetine, cephaeline	"	Chloroform—methanol—diethylamine (90:10:0.2)	"	15
Glaucine	LiChrosorb Si 60	n-Hexane—methanol—THF—diethylamine (88:5:4:0.15)	Fluorimetric $\lambda_1 = 310$ nm $\lambda_2 = 340$ nm	16
Cephaeline, emetine, ephedrine, morphine, and others	Silica gel S7 100	Diisopropyl ether—isopropanol—NH_4OH (48:0:2.08:3)	$\lambda_1 = 354, 356, 358$ nm $\lambda_2 = 476, 481, 492$ nm	17
Morphine in biological liquids	Spherisorb S3W	n-Hexane—isopropanol—NH_4OH (95:5:0.5)	$\lambda_1 = 350$ nm $\lambda_2 = 480$ nm	18
"	"	"	"	19a
		97:2.7:0.3	$\lambda_1 = 330\text{-}380$ nm $\lambda_2 = 410\text{-}500$ nm	

TABLE 2. (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Quinazoline Alkaloids				
Deoxyvasicinone, tetramethylenequinazolone	LiChrosorb Si-100	Ethyl acetate	UV (268 nm)	19b
Purine Alkaloids				
Caffeine, theobromine, theophylline, paraxanthine	LiChrosorb Si-60	Dichloromethane—formate buffer (965:35)	UV (280 nm)	20
Theophylline in serum	"	Dichloromethane—methanol—NH_4OH (95.8:4.0:0.2)	UV (270 nm)	21
Theophylline in plasma	LiChrosorb Si-60	Dichloromethane—ethanol—acetic acid—water (95.6:4:0.2:0.2	UV (275 nm)	22
Tropane Alkaloids				
Atropine, scopolamine	MicroPak Si-10	THF—diethylamine (100:1)	Refractometer	23
Cocaine isomers	Partisil 10 PXS	Heptane—isopropanol—diethylamine (75:25:0.1)	UV	24
Indole Alkaloids				
Ergot alkaloids	LiChrosorb Si-60	Chloroform—ethanol (95:5) or n-hexane—chloroform—ethanol (40:40:10)	UV (320 nm)	25
Ergocornine, α- and β-ergocryptines, ergocryptinine, ergocorninine, ergocristinine	"	Hexane—chloroform—acetonitrile (56:22:22)	"	26
Ergot alkaloids	Spherisorb W	Isooctane—dichloromethane—methanol (5:4:1)	Mass spectrometer	27
Ergometrine, ergotamine, ergocristine, ergocornine	LiChrosorb Si-60	n-Hexane—ethyl acetate—triethylamine—formamide (50:48:1:1)	UV (312 nm)	28
Vincamine, apovincamine, dehydrovincamine	MicroPak Si-10	n-Hexane—chloroform—methanol (60:30:10)	UV (280 nm)	29
"	LiChrosorb Si-60	(80:10:10)	"	"
Carbazole Alkaloids				
Glycozoline, glycozolidine, heptazolidine, koenimbine, koedidine, and others	μ-Porasil	n-Hexane—chloroform (7.5:2.5)	UV (254 nm)	30
Steroid Alkaloids				
Solanidine, rubijervine, veramine, solasodine, tomatine, jervine, cyclopamine, verarine	Zorbax-Sil	Hexane—methanol—acetone (18:1:1)	UV (213 nm)	31
Veratrine	μ-Porasil	Petroleum ether—ethanol—diethylamine (950:50:4)	UV (245 nm)	32
Alkaloids with an Exocyclic Nitrogen Atom				
Ephedrine, pseudoephedrine, methylephedrine	LiChrosorb Si-60	Hexane—ethanol—NH_4OH (125:76:1)	UV (220 nm)	33a

TABLE 2 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Liter- ature
Diterpene Alkaloids				
Indaconitine, chasmaconitine, talitizamine	Zorbax	Methanol—water—chloroform—triethylamine (70:30:1:0.1)	UV	33b

ence is given to chemically grafted phases, although the latter, as well, are not infrequently hydrolytically unstable.

HPLC OF ALKALOIDS ON SILICA GELS WITH CHEMICALLY GRAFTED PHASES

The use of silica gel with grafted phases was preceded by the method of dynamic modification in which the modifying agent is included in the composition of the mobile phase and interacts with the sorbent in the chromatographic process [1]. In this case, adsorption nevertheless played an important role. The stationary phase in the process of dynamic modification may be compared with a polar modifying agent in adsorption liquid chromatography (alcohol, ammonia).

Dynamic modification is not used at the present time, since silica gel with grafted phases (mainly with C_{18}) has practically displaced it, and the method bears the name of reversed-phase HPLC. This method makes it possible to obtain more reproducible separations. In reversed-phase chromatography, the choice of mobile phase is limited because of the high viscosity of polar solvents, and therefore mixtures of methanol and acetonitrile with water are generally used. These solvents dissolve practically all groups of alkaloids relatively readily and permit working over a wide UV range, since they are UV-transparent from 190-210 nm onward. Regions of absorption of the alkaloids of all groups lie above this value, and therefore preference is given to UV detection (Table 3).

Reversed-phase chromatography for the analysis of alkaloids using as the mobile phase mixtures of methanol and water and of acetonitrile and water has limited application. Thus, the opium alkaloids [82], caffeine [93], and the indole alkaloids [134] have been separated in an aqueous methanol mobile phase, and the ergot alkaloids [127] and formylephedrine [164], for example, in aqueous acetonitrile.

The addition to these mobile phases of buffer solutions with suitable pH values has enabled separation to be optimized and the range of groups of alkaloids capable of separation to be broadened: nicotine [34], purine alkaloids [89, 110], pyrrolizidine alkaloids [121, 122], indole alkaloids [144-146, 148-150], and steroid alkaloids [161a] have been separated in a methanol—phosphate buffer solution mobile phase; and isoquinoline alkaloids [63, 64, 68], quinolizidine alkaloids [126], indole alkaloids [143], and alkaloids with an exocyclic nitrogen atom (ephedrine) [162, 163] in an acetonitrile—phosphate solution as mobile phase. To increase dissolving power, a mixture of methanol, acetonitrile, and phosphate buffer solution has been used for the separation of isoquinoline alkaloids [71, 86, 87], indole alkaloids [151], and colchicine and its derivatives [165, 166]. An acetate buffer solution has proved useful for the separation of purine alkaloids [94-106] and also isoquinoline alkaloids [83], tropane alkaloids [112, 113], quinazoline alkaloids [120], and indole alkaloids [138-140].

A variant of ion-pair chromatography on a reversed phase has proved to be universal for the HPLC of alkaloids. In this case, a counter-ion the charge of which is opposite to that of the charge of the molecule of the substance to be chromatographed is added to the mobile phase (see Table 3).

In recent years, separations under the conditions of reversed-phase and ion-pair chromatography have been carried out with the use of silica gel having grafted-on cyano- and aminopropyl functional groups. These sorbents are more selective and are being used successfully for the analysis of alkaloids of various groups. The examples given in Table 4 are witnesses of this.

Thus, on silica gels with cyanopropyl groups it is possible to separate alkaloids of the pyridine [177], quinalozidine [170], quinoline [178], isoquinoline [174, 176, 181, 169,

TABLE 3. Reverse-Phase HPLC of Alkaloids

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Pyridine Alkaloids				
Nicotine	LiChrosorb RP-18	0.05 M $(NH_4)_2HPO_4$ (pH 7.5)—methanol (40:60)	UV (254 nm)	34
Nicotine, anatabine, anabasine, nornicotine	μ-Bondapak C_{18}	40% methanol containing 0.2% of H_3PO_4 + $(C_2H_5)_3N$ to pH 7.25	"	35
Nicotine, N-methylnicotininium ion	"	Mixture of A and B (92.5:6.5) (pH 3.0), A being a 2 mM solution of NaH_2PO_4 containing 0.25 mM Na octyl sulfate and B being methanol—acetonitrile (3:1)	Electrochemical	36
Nicotine in plasma	"	The same mixture in a ratio of 95:5	"	37
Capsaicins and piperine	"	Acetonitrile—phosphate buffer solution (45:55)	UV (340 nm)	38
			Electrochemical	39
Pyridoxyl alkaloids	"	Methanol—0.3% solution of Na dodecyl sulfate in 0.01 M H_3PO_4; gradient from (40:60) to (75:25) in 35 min	UV (290 nm)	39
Nicotine, cotinine	Nova-Pak C_{18}	Water—methanol (3.5:5.5) + 20 mM pentanesulfonic acid	UV (546 nm)	40
Quinoline Alkaloids				
Cinchonine, cinchonidine, quinidine, quinine	LiChrosorb RP-8	Acetonitrile—0.01 M KH_2PO_4 (15:85) (pH 3.0)	UV (254 nm)	41
	Nova-Pak C_{18}	Acetonitrile—0.1 M KH_2PO_4 (7:93) (pH 3.0)	"	
Quinoline and indole alkaloids	"	0.1 Phosphate buffer—acetonitrile (85:15) + 5 mM hexylamine	UV (275 nm)	42
Cinchonine, cinchonidine, quinidine, quinine	μ-Bondapak C_{18}	Methanol—water—acetic acid (25:75:1)	UV (254 nm)	43
Quinidine, quinine, cinchonine, dihydroquinidine, dihydroquinine	"	Methanesulfonic acid (1 M)—diethylamine (1M)—water—acetonitrile (20:20:860:100)	"	44
Quinidine sulfate, quinine hydrochloride, and quinine sulfate	Nucleosil C_{18}	Water—acetonitrile—methanesulfonic acid (43:5:1.1)	UV (235 nm)	45
Furo- and dihydrofuroquinoline alkaloids	μ-Bondapak C_{18}	$5 \cdot 10^{-3}$ M solution of pentanesulfonate in ethanol—water (30:70)	UV (254 nm)	46
Camptothecin and its analogs	Partisil-10 ODS-3C_{18}	Acetonitrile—water acidified with 0.1% of CF_3COOH	UV (270 nm)	47

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Isoquinoline alkaloids				
Oxymorphone, morphine, naltrexone, naloxone, nalorphine	μ-Bondapak C_{18}	Methanol—water (20:80) containing 50 mM tetramethylammonium hydroxide, + H_3PO_4 to pH 6.1	Amperometric	48
Coptisine, cryptopine, parfumine, protopine	Separon SG XC_{18}	Methanol—water—triethylamine (50:50:0.1)→ (80:20:0.1) in 10 min	UV (280 nm)	49
Morphine, normorphine	μ-Bondapak C_{18}	Methanol—water—NH_4OH (50:50:0.1)	Electrochemical	50
Papaverine, noscapine, heroin, procaine, codeine, morphine	Silica gel C_{18}	55% of citrate-TMA (0.01 M) buffer solution (pH 6.0), 28% of methanol and 17% of acetonitrile	Fluorimetric $\lambda_1 = 260$ nm $\lambda_2 = 400$ nm	51
Opium alkaloids	Silica gel RP-18	Acetonitrile—0.01 N $(NH_4)_2CO_3$ (4:6)	UV (240 nm) (340 nm)	52
Codeine	Polygosil C_{18}	Methanol—0.1 M $(NH_4)_2CO_3$ (70:30)	UV (220 nm)	53
Salutaridine, isothebaine, thebaine, orientalidine, oripavine, alpinigenine	LiChrosorb Supersphere RP-18	Isopropanol—acetonitrile—water—$(NH_4)_2CO_3$ (5:40:55:1)	UV (280 nm)	54
Codeine	LiChrosorb RP-18	0.5% solution of CH_3COONH_4 in methanol—water (70:30)	UV (212 nm)	55
Morphine, codeine, thebaine, papaverine, noscapine narceine	"	0.02 M methanesulfonic acid—methanol—dioxane—sulfuric acid (85:15:1:0.5) (pH 3.5)	UV (280 nm)	56
Morphine, codeine, 6-monoacetylmorphine	Spherisorb ODS	0.05 M solution of Na pentanesulfonate—acetonitrile (70:3)	UV (220 nm)	57
Morphine in rat brain	Spherisorb—Ultrasphere ODS	Methanol—buffer solution of 50 mM citric acid + 100 mM Na_2HPO_4 + 0.38 mM Na octyl sulnate + 0.5 EDTA (pH 4.2) (15:85)	UV (220 nm) Amperometric	58
Alkaloids in the cells of papaveraceous plants	Nova-Pak C_{18}	0.1 M solution of tartaric acid containing 0.125% of Na dodecyl sulfate—acetonitrile (45:55)	UV (285 nm)	59
Papaveraldine and papaverinol in preparations of papaverine	Silica gel RP-18	Water—methanol—acetonitrile containing 0.002 mM Na lauryl sulfate and 6 mM acetic acid (41:40:19)	UV (238 nm)	60
Morphine in poppy straw	μ-Bondapak C_{18}	0.1 M solution of NaH_2PO_4 in 6% aqueous acetonitrile	UV (240, 340 nm)	61
Morphine, codeine, thebaine in opium resin	"	0.1 M solution of NaH_2PO_4 in 5% aqueous acetonitrile	UV (254 nm)	62

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
pium alkaloids	Supelco LC-18	Acetonitrile—phosphate buffer solution (pH 5.05) (65:35), or acetonitrile—water (80:20)	UV and fluorometric	63
orphine and its derivatives	ID YMC AL-312 (ODS)	10 mM phosphate buffer solution (pH 6.8)—acetonitrile	UV (214 nm)	64
orphine, normorphine	μ-Bondapak C_{18}	8% of methanol + 5% of acetonitrile + 0.5 mM Na acetate + 0.12 M KH_2PO_4	Fluorimetric λ_1 = 210 nm λ_2 = 340 nm	65
eroin, monoacetylmorphine, cetylcodeine, noscapine, apaverine	Hypersil C_{18}	Methanol—phosphate buffer solution (pH 2.2 containing 0.023 M hexylamine. Gradient (5:95) → (30:70)	UV (218, 228, 240 nm)	66
orynoline, 13-epicorynoline, 1-epicorynoline, acetyl-orynolin	IWG-C_{18}	Methanol—water containing 0.017 M KH_2PO_4 (70:30)	UV (289 nm)	67
oscapine	μ-Bondapak C_{18}	Acetonitrile—KH_2PO_4 (45:55) brought to pH 3 with H_3PO_4	UV (254, 230 nm)	68
oscapine, narcotoline, otarnine	Nucleosil C_{18}	Acetonitrile + phosphate buffer solution + an aliphatic tertiary amine in various concentrations, pH 2	UV (210 and 310 nm)	69
Allocryptopine, protopine, helidonine	LiChrosorb RP-18	Methanol—buffer solution (pH 7.0)—di(2-ethylhexyl) orthophosphate	UV (280 nm)	70
Glaucine	μ-Bondapak C_{18}	Methanol—acetonitrile—0.05 M phosphate buffer solution (4:1:5)	UV and refractometric	71
Morphine, codeine, thebaine, narceine, narcotine, papaverine in plant materials	Nucleosil-5 C_{18}	Acetonitrile—0.05 M phosphate buffer solution (30:70) containing 0.005 M Na octanesulfonate (pH 3)	UV (220 nm)	72
Morphine, codeine, noscapine, papaverine	μ-Bondapak C_{18}	Methanol—water (34:65) containing 0.05 M phosphate buffer and 0.005 M camphorsulfonic acid (pH 3)	UV (254 nm)	73
Morphine, codeine, apomorphine, pseudomorphine	Hypersil ODS	Acetonitrile—water containing 100 mM Na lauryl sulfate and 40 mM NaH_2PO_4 (pH 3)	UV (254 nm)	74
Morphine in blood serum	Ultrasphere ODS	Aqueous solution containing solution 0.1 M NaH_2PO_4, 0.002 M octanesulfonic acid, and 0.001 M disodium salt of EDTA—methanol (3:1)	Electrochemical	75
Morphine and metabolites	Apex ODS	10 mM NaH_2PO_4 (pH 2.1) + 1 mM Na dodecyl sulfate + 26% of acetonitrile	Fluorimetric	76

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Diamorphine, morphine	Hypersil ODS	0.1 M Na pentanesulfonate—acetonitrile—H_3PO_4 (pH 2) (69.5:30:0.5)	UV (284 nm)	77
Tetrahydropapaveroline and its metabolites	Supelcoport	0.05 M solution of $NH_4H_2PO_4$ containing 0.75 mM triethylamine, 0.05 mM Na pentanesulfonate and 4.6% of 1,4-dioxane (pH 4.5)	Electro-chemical	78 79
Emetine, cephaeline	μ-Bondapak C_{18}	1 g of Na heptanesulfonate + 400 ml of methanol + 1 ml of H_3PO_4 + water to 1 liter	Flourimetric $\lambda_1 = 276$ nm $\lambda_2 = 304$ nm	80
Remerine, glaucine, dehydroremerine, dehydroglaucine, mecambrine, amurine	"	Acetonitrile—water—triethylamine (40:60:0.1)	UV (280 nm)	81a
R- and S-Salsolinols	Nova-Pak C_{18}	Methanol—50 mM phosphate buffer (pH 3.0) (55:45)	Electro-chemical	81b
Morphine, codeine, thebaine, noscapine, papaverine, laudanosine, cryptopine, narceine, and meconic acid in gum opium	Nucleosil 7 C_6H_5	Gradient of A [0.7 M triethylammonium phosphate (1 ml)—methanol—water (35:95), pH 3.2]; and B [methanol—water (70:30)—0.7 M triethyl-ammonium phosphate (1 ml), pH 3.95] (100:0)→(0:100) A:B A:B	UV (280 nm)	82
Apomorphine and N- and propylnorapomorphines in plasma	μ-Bondapak Ph	40% of methanol + 60% of (0.02 M CH_3COONa—0.03 M CH_3COOH), pH 3.25	Fluorimetric $\lambda_1 = 281$ nm $\lambda_2 = 418$ nm	83
Morphine, normorphine, codeine	Spherisorb Ph	Mixture of 0.1% of TFA in water and 0.1% of TFA in 40% acetonitrile	$\lambda_1 = 280$ nm $\lambda_2 = 335$ nm	84
Morphine, codeine, papaverine, thebaine, and noscapine in gum opium	μ-Bondapak Ph	Methanol—1% CH_3COONa containing 7.0 mM trimethylamine (58:42)	UV (254 nm)	85
Codeine, morphine, norcodeine	Spherisorb Ph	Acetonitrile—methanol—$2.5 \cdot 10^{-2}$ M phosphate buffer solution (pH 2.8) (7:2:91)	Amperometric	86 87
Purine Alkaloids				
Theophylline, caffeine, and others	LiChrosorb C_8	Acetate buffer solution (pH 4)—ethanol (92:8)	UV (254 nm)	88
Theophylline, theobromine, caffeine	LiChrosorb RP-9	Methanol—water—0.2 M phosphate buffer solution (pH 5.0) (9:36:5)	UV (275 nm)	89
Theophylline	"	10 mM CH_3COONa + 0.005 M tetrabutylammonium phosphate with 4% of methanol + CH_3COOH to pH 4.5	UV (273 nm)	90

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
	LiChrosorb RP-8	Methanol—phosphate buffer solution (pH 6.0) (7:93) + 7.8 mM N,N-dimethyl-M-octylamine	UV (254 nm)	91
Caffeine and theophylline and their metabolites	Hypersil ODS	Gradient: 0→12.75% of acetonitrile in 1% THF (pH 4.8)	UV (280 nm)	92
Caffeine	μ-Bondapak C_{18}	Methanol—water (30:70)	UV (273 nm)	93
"	"	5% acetic acid	UV (254 nm)	94
Theobromine	Ultrasphere ODS	10 mM acetate buffer solution (pH 4.5)	UV (275 nm)	95
Theophylline, theobromine, caffeine	Micro-B ODS-3	Water—methanol—acetic acid (68:31:1)	UV (280 nm)	96
Theobromine, paraxanthine, theophylline, caffeine	Bond-Elut C_{18}	1% acetic acid—methanol (83:17)	UV (273 nm)	97
Caffeine	Supelcosil C_{18}	0.5% acetic acid—methanol (20.5)	UV	98
"	Partisil PX 10/25 ODS-2	Acetonitrile—acetic acid—water (25:5:75)	UV (275 nm)	99
Caffeine, theophylline, theobromine, paraxanthine, others	Perkin—Elmer C_{18}	Water—isopropanol—acetonitrile—acetic acid (91:4:4:1)	UV (276 nm)	100
Theophylline	Hypersil ODS	1.28 g/liter of CH_3COONa + 20% of acetonitrile and 0.5% of acetic acid	UV (280 nm)	101
"	Novapak-C_{18}	0.01 M acetate buffer (pH 4.0) + 6% of acetonitrile	UV (280 nm)	102
Theophylline, diphylline	Partisil PX 50/25 ODS-2	7% of methanol and 1% of THF in 0.01 M acetate buffer solution (pH 5)	"	103
Theophylline, ephedrine	μ-Bondapak C_{18}	Buffer solution [0.1% of aq. $(NH_4)_2CO_3$ + CH_3COOH to pH 7.0]—acetonitrile [1:1]	UV (254 nm)	104
Theophylline and caffeine in biological materials	Spherisorb C_{18}	0.05 M acetate buffer (pH 5.0)—acetonitrile (93:7)	UV (280 nm)	105
Caffeine	Hypersil ODS	0.1 M CH_3COONH_4 (pH 4.6)—acetonitrile (83:15)	"	106
Theophylline	Spherisorb C_{18}	n-Hexanoic acid (0.006 M)—acetonitrile (86:14)	UV (276 nm)	107
Theophylline, theobromine, caffeine, and others	Ultrasphere C_{18}	0.02 M tetrabutylammonium ion and 0.015 M Tris buffer in H_2O—CH_3CN—CH_3OH (93:3.5:3.5)	UV (280 nm)	108
Theophylline, theobromine, caffeine	LC-18DB	1.75 mM H_3PO_4—CH_3CN—THF (97:0.2:0.1)	UV (273 nm)	109

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Theophylline	Sepralyte C_{18}	0.05M $NH_4H_2PO_4$ + 0.01 M H_3PO_4 + DMFA (1%), + 4% of CH_3OH	UV (276 nm)	110
Caffeine, theobromine, theophylline	Spherisorb Ph	20% of CH_3OH in 20 mM phosphate buffer brought to pH 5.6 with the aid of 8% H_3PO_4	UV (273 nm)	111
Tropane Alkaloids				
Hyoscyamine, scopolamine, atropine	μ-Bondapak C_{18}	3% $CH_3COOH—CH_3OH$ (7:3)	UV (254 nm)	112
Benzoylecgonine	"	Water—methanol—acetic acid (86:13:1)	"	113
Homatropine	"	Methanol—water (1:9) (1 liter) + 25 ml of sodium heptanesulfonate	UV (235 nm)	114
Cocaine, norcocaine, benzoylecgonine, benzoylnorecgonine	Velosep ODS	0.01 M phosphate buffer + 0.02 TBA-OH + 6% of CH_3CN (pH 2.1)	UV (233 nm)	115
Hyoscyamine, scopolamine, anisodamine, anisodine	Silica gel ODS	1/15 M Na_3PO_4 (pH 3.5)—methanol (48:52) + 17.5 mM Na dodecyl-sulfate	UV (210 nm)	116
Quinazoline Alkaloids				
Vasicine, deoxyvasicinone	LiChrosorb C_{18}	Gradient: 10% methanol—aq. $HClO_4$ (pH 1.24) + 2% of methanol per minute	UV (254 nm)	117
Vasicine, and its analogs	μ-Bondapak C_{18}	Methanol—water (70 ml + 30 ml) containing 1 ml of hexanesulfonic acid	"	118
Vasicine, vasicinone	Apex ODS	Methanol—dichloromethane—$HClO_4$ (50:50:0.01)	UV (300 nm)	119
"	Nucleosil C_{18}	Acetonitrile—water—acetic acid	"	120
Pyrrolizidine Alkaloids				
	μ-Bondapak C_{18}	Methanol—0.01 M KH_2PO_4 (30:70)	UV (219 nm)	121
Intermedine, lycopsamine, sincamidine, seneciphylline, senecionine, jacobine, jacoline, jaconine	Semiprep C_{18}	Methanol—0.01 M KH_2PO_4 (17.5:82.5), pH 4.79	UV (218 nm)	122
Macrocyclic pyrrolizidine alkaloids	Cosmosil 5 Ph	Methanol—0.02 M $(NH_4)_2CO_3$ (45:55), pH 8.2	UV (215 nm)	123
Imidazole Alkaloids				
Pilocarpine, isopilocarpine	Radial-Pak C_{18}	2-Aminopropane—methanol—2 M H_3PO_4—0.15 M Na_2SO_4 (8.7:14.6:22.0:54.7)	UV (220 nm)	124

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Pilocarpine hydrochloride, isopilocarpine, pilocarpic acid, isopilocarpic acid	μ-Bondapak Ph	5% KH_2PO_4 brought to 2.5 with the aid of H_3PO_4	UV (215 nm)	125
Quinolisidine Alkaloids				
Lupinine, lusitanine, matrine, sophoridine, sophocarpine, sparteine, lupanine, anagyrine, and others	Inertsil ODS	Acetonitrile—5 mM phosphate buffer (pH 5.5) (1:9)	UV (310 nm)	126
Indole Alkaloids				
Ergot alkaloids	Kieselgel C_{18}	Acetonitrile—water (55:45)	UV (254 nm)	127
Harmine, harmol, harmaline, harmalol	LiChrosorb RP-18	Methanol—water—formic acid (16:34:1)	Fluorimetric $\lambda_1 = 304$ nm $\lambda_2 = 355$ nm	128
Vincamine, apovincamine, dehydrovincamine	μ-Bondapak C_{18}	Acetonitrile—0.01 M $(NH_4)_2CO_3$ (4:6), (6:4), and (7:3)	UV (280 nm)	129 130
Ergot alkaloids	LiChrosorb RP-8	Acetonitrile—0.01 M $NaHCO_3$ (42:58)	UV	131
Vincamine, apovincamine	μ-Bondapak C_{18}	Methanol—0.01 M $(NH_4)_2CO_3$ (75:25)	UV (254 nm)	132
Ergotamine, ergotaminine, ergocrystine	Hypersil ODS	Acetonitrile—0.01 M $(NH_4)_2CO_3$ (30:70)	Fluorimetric $\lambda_1 = 328$ nm $\lambda_2 = 389$ nm	133
Heteroyohimbine, ajmalicine, and others	Spherisorb ODS	Methanol—water (80:20); methanol—water—NH_4OH (80:20:1)	UV (254 nm)	134
Vobasine, perivine, apparicine, and others	LiChrosorb RP-18	0.02 M methanesulfonic acid—dioxane—sulfuric acid (95.5:5:0.5) (pH 4)	UV (280 nm)	135
Dihydroergocornine, dihydroergocryptine, and others	"	Water—acetonitrile—triethylamine (220:50:0.2)	UV (281 nm)	136
	Spherisorb RP-18	" 645:336:190	UV (280 nm)	137
Ergocornine, α- and β-ergocryptines	LiChrosorb RP-18	THF—0.01 M CH_3COONH_4 (4:6)	Fluorimetric $\lambda_1 = 280$ nm $\lambda_2 = 322$ nm	138
Ajmalicine, serpentine, catharamphine, tabersonine	μ-Bondapak C_{18}	Acetonitrile—0.1 M CH_3COONH_4 (51:49), pH 7.2	UV (280 nm)	139
Physostigmine	Spherisorb ODS	Acetonitrile—0.01 M CH_3COONa (95:5)	Fluorimetric $\lambda_1 = 254$ nm $\lambda_2 = 346$ nm	140
"	"	0.01 M octanesulfonic acid + 1% of CH_3COOH→ CH_3CN—H_2O (52:48), pH 3.5)	UV (254 nm)	141
Yohimbine	μ-Bondapak C_{18}	Acetonitrile—$1.2 \cdot 10^{-3}$ M HCl—methanol (60:10:30)	UV (280 nm)	142

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Vincamine	Spherisorb ODS	Acetonitrile—0.02 M K_3PO_4 (pH 2.3) (50:50)	UV (230 nm)	143
Ajmalicine, serpentine, catharanthine, vindoline, tryptamine, vinblastine	μ-Bondapak C_{18}	Methanol—5 mM $(NH_4)_2HPO_4$ (pH 7.3)	UV (254 nm)	144
Yohimbine	"	Water—methanol (52:48) containing 0.01 M $(NH_4)_2PO_4$	Electrochemical	145
Lysergic acid, lysergamide, lysergide, ergosine, ergotamine, and others	Hypersil ODS	Methanol—water (60:40) containing phosphate buffer (pH 8.1)	UV (220 nm)	146
Ajmaline, reserpine, rescinnamine	LiChrosorb RP-18	Phosphate buffer—acetonitrile—n-propanol—THF (70:13:13:4)	UV (292 nm)	147
Vincristine, vinblastine	"	Methanol—water (85:15) containing 3 mM H_3PO_4 and 0.5 mM KH_2PO_4	UV (222 nm) Fluorimetric $\lambda_1 = 226$ nm $\lambda_2 = 340$ nm	148
Vinblastine, vincristine, vindesine	Hypersil ODS	Methanol—10 mM phosphate buffer (pH 7.0) (65:35)→(55:45)	Electrochemical	149
Harman	Spherisorb S5 ODS1	Acetonitrile—ethanol—0.02 M phosphate buffer (pH 7.2) (39:13:48)	Fluorimetric $\lambda_1 = 238$ nm $\lambda_2 = 435$ nm	150 151
Harmine	"	30:30:40	$\lambda_1 = 244$ nm $\lambda_2 = 425$ nm	151
Harmaline	"	40:30:30	$\lambda_1 = 374$ nm $\lambda_2 = 485$ nm	151
Psilocybin, psylocin	μ-Bondapak alkylphenyl	Methanol—water (35:65) containing 0.5 M heptane-1-sulfonic acid, pH 3.5	UV (267, 254, 290 nm)	152
Perivine, tabernaemontaine, vobasine, apparicine, and others	μ-Bondapak Ph	6.8 g/liter of NaH_2PO_4 (pH 3.9)—acetonitrile—2-methoxyethanol (80:15:5)	UV (275, 313 nm)	153
Diterpene Alkaloids				
C_{19}-Diterpene alkaloids	Silica gel C_{18}	THF—17 mM $(NH_4)_2CO_3$ (1:1)	UV (254 nm)	154
Lappaconitine	μ-Bondapak C_{18}	0.5% CH_3COONH_4—THF—methanol—acetonitrile (73:3:2:1)	"	155
Mesaconitine, aconitine, benzoylaconine, and others	TSK gel ODS	0.05 M phosphate buffer (pH 2.7)—THF (89:11)	"	160
Carbazole Alkaloids				
Ellipticine	μ-Bondapak C_{18}	Methanol—water (60:40) containing 100 ml/liter of CH_3COONH_4 (pH 6)	Electrochemical	156

TABLE 3 (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Solasonine, solasodine, solasodiene	"	Acetonitrile—0.01 M Tris buffer (70:30)→(40:60)	UV (205 nm)	157
α-Solanine, β-solanine, γ-solanine, α-chaconine, β-chaconine, γ-chaconine, solanidine	Radial-Pak C_{18}	Acetonitrile—water—ethanolamine (50:50:0.2)	UV (200 nm)	158
Veratrine, veratridine	μ-Bondapak C_{18}	Methanol—0.1 M CH_3COONH_4 (pH 5.5) (60:40)	UV (220 nm)	159a
Solanidine, demissidine, leptinidine, tomatidine, solasodine, and others	Supelcosil LC-18DB	Acetonitrile—methanol—ethanolamine (60:40:0.001)	Refractometer	159b
α-Solanine, α-chaconine	Hypersil ODS	Methanol—water—H_3PO_4 (95:30:0.1)	UV (205 nm)	161a
Extract of Funtumia africana	μ-Bondapak C_{18}	Methanol—water—Low UV PIC B7 (20:80:2)	UV (240 nm)	161b
Alkaloids with an Exocyclic Nitrogen Atom				
Ephedrine	Silica gel C_8	Acetonitrile—0.01 M KH_2PO_4 (pH 3.0) (10:90)	UV (214 nm)	162
Ephedrine, pseudoephedrine, norephidrine	Ultrasphere ODS	Acetonitrile—water (400 ml: 600 ml) + 1.4 g of $NH_4H_2PO_4$	UV (254 nm)	163
Formylnorephedrine in plasma	μ-Bondapak C_{18}	Acetonitrile—water (1:4)	UV (256 nm)	164
Colchicine and its derivatives	LiChrosorb RP-18, RP-8	Methanol—acetonitrile—phosphate buffer (pH 6) (5:16:79)	UV (350 nm)	165
Colchicine	Radial-Pak C_{18}	Acetonitrile—methanol—0.025 M phosphate buffer (pH 5.6) (26.25:8.75:65)	"	166
Colchicine, demicoline, N-deacetylcolchicine	Microsorb C_{18}	0.1 M KH_2PO_4—methanol—acetonitrile (60:26.6:13.4) + 5 mM pentane-1-sulfonic acid + 0.1 M KOH to pH 6.0	UV (254, 350, nm)	167

168] and indole [175] series and alkaloids with an exocyclic nitrogen atom [173, 182], while alkaloids of the isoquinoline [179], indole [180], and steroid [161a, 171, 172] series are separated on silica gels with aminopropyl groups.

The method of ion-pair chromatography occupies an intermediate position between ion-exchange chromatography and adsorption, partition, or reversed-phase chromatography. The method is fairly useful and its advantage in comparison with classical ion-exchange chromatography is that the active centers are fixed. Thanks to the fast mass transfer in the ion-pair system, chromatographic separation is more effective than on an ion-exchange resin with fixed and active zones. The disadvantages of ion-exchange resins include lack of reproducibility from batch to batch, lower activity and stability as compared with other sorbents, and a small variety, which limits the use of ion-exchange chromatography for the separation of alkaloids.

In conclusion, it must be mentioned that the possibilities of HPLC are unlimited, and in spite of the fact that the choice of the optimum conditions of separation in the light

TABLE 4. HPLC of Alkaloids on Silica Gels with Grafted-on Cyano- and Aminopropyl Groups

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
Pyridine Alkaloids				
Piperine	μ-Bondapak CN	Methanol—water (50:50)→(80:20)→ 100% methanol	UV (28 nm)	177
Quinoline alkaloids				
Quinine, quinidine, cinchonidine, cinchonine	Spherisorb CN	(0.0068 M H_3PO_4 + 1 M NaOH to pH 7) —acetonitrile—methanol—THF (50:17:28.7:3.3)	UV (231 nm)	178
Isoquinoline Alkaloids				
Codeine, norcodeine, morphine	"	Acetonitrile—triethylamine—water (4:0.1:95.9) containing 2 M H_3PO_4 to pH 3.1	Fluorimetric λ_1 = 230 nm λ_2 = 350 nm	168
Morphine, codeine, cryptopine, thebaine, narcotine, papaverine	Nucleosil 10 CN	1% CH_3COONH_4—acetonitrile—dioxane (80:10:10)	UV	181
Morphine, pseudomorphine	μ-Bondapak CN	0.05 M KH_2PO_4 (pH 4.5)—acetonitrile (80:20)	UV (240 nm)	176
Apomorphine in plasma	μ-Bondapak CN	Acetonitrile—0.02 M KH_2PO_4 (11:89) containing 0.5 mM EDTA + H_3PO_4 to pH 3	Electrochemical	174
D-Tubocurarine chloride in plasma	Radial-Pak CN	Acetonitrile—methanol—water—1.0 dibutylamine phosphate (pH 2.5) (40:10:10:1)	UV (204 nm)	169
Morphine, codeine, thebaine, papaverine, narceine	Zorbax NH_2	Acetonitrile—0.025 M KH_2PO_4 (75:25)	UV (286 nm)	179
Alkaloids with an exocyclic nitrogen atom				
Ephedrine, methylephedrine, norephedrine, pseudoephidrine	Zorbax CN	0.0009 M dibutylamine phosphate (pH 2.2)	UV (210 nm)	182
Pseudoephedrine in plasma	LiChrosorb CN	Methanol—water—acetonitrile—KH_2PO_4—Na pentanesulfonate—Na hep-tanesulfonate (20:800:160:10:1:1)	UV (205 nm)	173
Quinolizidine Alkaloids				
Sparteine and its metabolites	Spherisorb CN	Acetonitrile—methanol—phosphate buffer (pH 2.5) (25:32:43)	Electrochemical	170
Indole Alkaloids				
Vinblastine, vindesine, vincristine	LiChrosorb CN	Acetonitrile—phosphate buffer (pH 3.0) (65:35)	UV (220 nm)	175
Ergocristine, ergocristinine, and others	LiChrosorb CN	Ethanol—ether (4:96)	"	180
Steroid Alkaloids				
α-Solanine, α-chaconine	μ-Bondapak NH_2	Ethanol—acetonitrile—0.005 M KH_2PO_4 (3:2:1)	UV (205 nm)	161a

TABLE 4. (continued)

Alkaloid	Stationary phase	Mobile phase	Detector	Literature
α-Chaconine, α-solanine, β-chaconine, γ-chaconine, β-solanine	Radial-Pak NH_2	THF—acetonitrile—water—methanol (55:30:10:5)	UV (215 nm)	171
α-Solanine, α-chaconine	Nucleosil 5-NH	Acetonitrile—20 mM KH_2PO_4 (75:25)	UV (208 nm)	172

of the possible mechanism of the interactions of the sorbents and alkaloids being analyzed is still a problem for the development of separation procedure, the results available are bringing us closer to the solution of this problem.

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FATTY-ACID AND PHOSPHOLIPID COMPOSITION OF LICHENS OF THE VOLGA BASIN

V. M. Dembitskii, I. A. Bychek,
M. V. Shustov, and O. A. Rozentsvet

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The composition of the fatty acids and phospholipids of 16 species of lichens collected in the basin of the river Volga has been studied. The main phospholipid was phosphatidylcholine the amount of which ranged in the various species from 33.3 to 85.5% of the total phospholipids. Other phospholipids were also found: phosphatidylethanolamine, phosphatidylserine, phosphatidylinositol, and phosphatidylglycerol. The main fatty acids were the 16:0, 18:0, and 18:1 varieties.

The fatty acids (FAs) in phospholipids (PLs) of lichens have been little studied [1-7]. The lipids of lichens growing on the territory of the USSR, including the Volga basin, have not been studied previously. The main class of PLs in all the species studied was phosphatidylcholine, its amount ranging from 33.3 to 85.5% (Table 1). The highest concentrations of PCs were observed for the family Cladoniaceae. Phosphatidylinositol was found in 10 species of these studies (6.8-33.9%). Phosphatidylserine was detected in only five species, in small amounts except for Anaptychia ciliaris in which its amount was 13.9%. In the family Cladoniaceae, PC (9.9%) was found in only one species – Cladonia sp. 4. In seven

TABLE 1. Phospholipid Compositions of Lichens

<table>
<tr><th>Species</th><th>PI</th><th>PS</th><th>PC</th><th>PE</th><th>PG</th><th>X</th><th>L</th></tr>
<tr><td>Anaptychia ciliaria</td><td>—</td><td>13,9</td><td>61,1</td><td colspan="2">16,7</td><td>8,3</td><td>18,6</td></tr>
<tr><td>Aspicilia transbaicalica</td><td>32,2</td><td>2,0</td><td>33,3</td><td colspan="2">30,4</td><td>—</td><td>30 6</td></tr>
<tr><td>Diploschistes sp.</td><td>—</td><td>—</td><td>58,2</td><td colspan="2">41,8</td><td>—</td><td>18,3</td></tr>
<tr><td>Evernia mesomorpha</td><td>24,6</td><td>—</td><td>59,4</td><td>13,3</td><td>2,7</td><td>—</td><td>16,5</td></tr>
<tr><td>Evernia prunastri</td><td>14,5</td><td>—</td><td>63,3</td><td colspan="2">21,9</td><td>—</td><td>13,4</td></tr>
<tr><td>Hypogimnia physodes</td><td>13,9</td><td>4,7</td><td>46,6</td><td>18,6</td><td>16,2</td><td>—</td><td>15,8</td></tr>
<tr><td>Lassallia pensylvanica</td><td>6,8</td><td>4,1</td><td>47,9</td><td>16,5</td><td>13,7</td><td>11,0</td><td>10,7</td></tr>
<tr><td>Umbilicaria deusta</td><td>33,9</td><td>—</td><td>37,8</td><td colspan="2">28,3</td><td>—</td><td>34,6</td></tr>
<tr><td>Cladonia sp. 1</td><td>—</td><td>—</td><td>85,5</td><td>9,7</td><td>4,8</td><td>—</td><td>33,6</td></tr>
<tr><td>Cladonia sp. 2</td><td>—</td><td>—</td><td>61,4</td><td colspan="2">36,8</td><td>1,8</td><td>28,4</td></tr>
<tr><td>Cladonia sp. 3</td><td>20,6</td><td>—</td><td>44,1</td><td>22,1</td><td>13,2</td><td>—</td><td>30 2</td></tr>
<tr><td>Cladonia sp. 4</td><td>—</td><td>9,9</td><td>56,2</td><td>23,1</td><td>10,8</td><td>—</td><td>22,1</td></tr>
<tr><td>Cladonia sp. 5</td><td>—</td><td>—</td><td>73,9</td><td>12,3</td><td>13,8</td><td>—</td><td>24,8</td></tr>
<tr><td>Cladonia sp. 6</td><td>—</td><td>—</td><td>72,2</td><td>11,1</td><td>16,7</td><td>—</td><td>34,2</td></tr>
<tr><td>Cladonia sp. 7</td><td>—</td><td>—</td><td>80,8</td><td colspan="2">19,2</td><td>—</td><td>20,9</td></tr>
<tr><td>Cladonia sp. 8</td><td>8,6</td><td>—</td><td>69,0</td><td>15,5</td><td>6,9</td><td>—</td><td>18,8</td></tr>
</table>

Abbreviations. PI) Phosphatidylinositol; PS) phosphatidylserine; PC) phosphatidylcholine; PE) phosphatidylethanolamine; PG) phosphatidylglycerol; X) unidentified polar PL; TL) total lipids, mg/g of dry tissue.

Institute of the Ecology of the Volga Basin, Russian Academy of Sciences, Tol'yatti.
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