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LIPIDS FROM ÉKDISTEN PRODUCTION WASTES

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The lipids and the fatty-acid composition of the wastes from the production of the drug Ékdisten from the roots and rhizomes of Rhaponticum carthamoides *have been studied. The lipids have been found to contain, predominantly, free fatty acids, including the 18:2 acid, and free and bound sterols and triterpenols. The desirability of using the wastes as a bioadditive in phytocosmetic preparations has been substantiated.*

Rhaponticum carthamoides (Willd.) Iljin., fam. Asteraceae, is a medicinal plant growing mainly in Western and Eastern Siberia and Central Asia [1]. Galenical preparations from the roots and rhizomes of *Rh. carthamoides* possess a tonic and adaptogenic effect [2], and the drug ékdisten an anabolic action [3].

The roots and rhizomes of *R. carthamoides* contain more than 3% of neutral lipids, while the analogous organs of other medicinal plants, such as *Inula helenium* L. (fam. Asteraceae), *Rubia tinctorum* L. (fam. Rubiaceae), and *Valeriana officinalis* L. (fam. Valerianaceae) contain 0.63-1.8% [4].

In the production of Ékdisten, the lipids and accompanying lipophilic compounds are concentrated in the form of wastes at a certain technological stage. Since many classes of plant lipids possess biological activity, such wastes may be of interest for medicine and phytocosmetics, and also domestic chemistry.

We have investigated the compositions of the lipids and lipophilic substances of the liquid and solid wastes formed in the processing of the roots and rhizomes of *R. carthamoides*. The liquid wastes are chloroform extracts of the ballast substances from concentrated alcoholic extracts, and the solid wastes are residues of the plant biomass after its extraction treatment [3].

The amount of hydrophobic substances in the liquid waste after the chloroform had been driven off was 1.54% of the weight of the initial raw material, while the yield of extractive substances from the solid residue (the extractant being chloroform—methanol) was 0.13%.

According to TLC in systems 1-9, the qualitative compositions of the lipids of the two types of wastes were identical. By CC, followed by preparative TLC in systems 1-7, we separated the mixture of substances from the liquid waste into individual fractions (Table 1).

The neutral lipids (NLs), like the sum of the tanning substances and flavonoids, amounted to 30-33% of the weight of the evaporated residue, the remainder being unidentified substances, including dark brown pigments.

Of polar lipids we detected only traces of glycolipids; according to the results of qualitative determinations, phospholipids were absent. It must be mentioned that the detection of phospholipid spots on chromatograms was made difficult by the superposition of the extended spot of the dark brown pigments.

In the NLs of the wastes, free fatty acids (FAs) and a mixture of phytosterols with triterpenols in the free and bound forms predominated.

We determined the component compositions of several classes of the NLs. According to TLC results (R_f 0.9-0.4, system 5), the hydrocarbons were represented by two groups of compounds. The first group was identified from its UV, IR, and mass spectra as paraffins of the C_{16}-C_{24} homologous series (M^+ 226-338), the main components being the C_{16}-C_{18} alkanes. On the basis of the absorption of the fraction in the UV spectrum at 229 nm and of diagnostic ions in the mass spectrum with *m/z* 91, 105, 119, and 133, the second group was assigned with some degree of confidence to the arylalkadienes of the general formula C_nH_{2n-10} [5, 6]. Their mixture included eight homologues, $C_{17}H_{24}$-$C_{24}H_{38}$, with a predominance of the C_{17}-C_{20} components.

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TABLE 1. Composition of the Waste from the Processing of the Roots and Rhizomes of *Rhaponticum carthamoides*, %

Class of substances	Amount
1. Hydrocarbons	2.0
2. Unidentified	0.3
3. Esters of fatty acids with sterols and triterpenols	4.4
4. Fatty acid ethyl esters	1.0
5. Triacylglycerols	3.6
6. Unidentified	2.5
7. Yellow pigments	0.9
8. Free fatty acids	6.6
9. Alkanols	4.0
10. Triterpenols and sterols	3.3
11. Diacylglycerols	2.3
12. Monoacylglycerols	1.8
13. Tanning substances	1.6
14. Flavonoids	27.6
15. Unidentified dark brown pigments	38.1

According to their mass spectra, the phytosterols from the *R. carthamoides* waste consisted of a mixture of β-sitosterol (M^+ 414, 100%) with stigmasterol, Δ^7-avenasterol (M^+ 412, 50%), campesterol (M^+ 400, 18%), and cholesterol (M^+ 386, 10%) [7]. The same mixture of phytosterols is bound with FAs in esters. The small alkanol residue of the other esters is, most probably, ethanol.

Glycolipids present were mono- and diagalactosyldiacylglycerols and steryl glycosides and their esters with FAs.

According to the results of GLC and mass spectrometry, the total acyl-containing lipids had the following set of FAs (%): 12:0-2.1, 13:0-1.4, 14:0-1.5, 15:0-1.3, 16:0-35.8, 16:1-7.4, 17:0-0.9, 18:0-2.1, 18:1-10.9, 18:2-33.1, 18:3-3.5. The sum of the unsaturated FAs made up almost 55%, and the proportion of the essential 18:2 and 18:3 FAs about 40% of the weight of the *R. carthamoides* acids.

Thus, half of the weight of the lipids present in the initial raw material is concentrated in the liquid waste from the processing of the roots and rhizomes of *R. carthamoides*, and these are enriched with essential FAs, mainly the 18:2 acid.

The majority of the classes of lipids in the waste from the processing of the roots and rhizomes of *R. carthamoides* possess a positive biological action. Thus, the FAs and their derivatives (esters with mono- and trihydric alcohols) exhibit antimicrobial, antifungal, and anticaries activities [8], while the 18:2 and 18:3 unsaturated acids are known as vitamins of the F group [9]. An antiviral activity has been revealed in monoacylglycerols [10] and alkanols [8], and hypolipidemic properties in triterpenoids [11] and β-sitosterol [12]. As is known, many flavonoids are antioxidants and are capable of structurally modifying lipids [13, 14].

Peculiar physicochemical properties have been detected in some lipid components. The biological activity of phytosterols is determined by their capacity for forming stable complexes with alcohols, phenols, acids and their derivatives and with amines, hydrocarbons, and proteins [15]. Monoacyl- and diacylglycerols, glycolipids, and FAs possess pronounced surface-active properties and constitute a group of nontraditional surface-active agents used for this purpose in pharmacology and phytocosmetics and in the textile and food industries [16].

Thus, the chemical results show the desirability of using the liquid waste from the processing of the roots and rhizomes of *R. carthamoides* as a biologically active additive, especially for hair care [17].

The utilization of wastes from medicinal plants enriched with bioactive lipids will permit the degree of processing of valuable plant biomass to be increased, the profitability of the production of drugs to be raised, and the process to be made ecologically purer, and it will provide the possibility of expanding the variety of phytocosmetics with new properties and user qualities. At the present time, a shampoo in the Aimonchiki children's range, which contains a lipid preparation of *R. carthamoides* waste as a bioadditive, is being produced commercially.

EXPERIMENTAL

The conditions for recording UV, IR, and mass spectra and for performing GLC and CC, and methods for the detection of individual lipid classes in TLC and for the isolation and identification of FAs have been described in [18]. Samples of the wastes after the isolation of Ékdisten from the plant biomass were taken in the Experimental Factory of the Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan.

TLC was conducted in the systems: hexane—diethyl ether: 1) (4:1); 2) (4:7.5); 3) (7:8); 4) (7:3); and 5) (99:1); hexane—diethyl ether—CH_3COOH; 6) (90:10:1); 7) (70:30:1); 8) chloroform—methanol—NH_4OH (65:25:5); 9) chloroform—acetone—methanol—CH_3COOH—H_2O (60:20:10:10:3).

Paraffins were eluted from the column with hexane. White grease-like substance, R_f 0.9 (system 5). Not revealed with I_2 vapor. UV spectrum (hexane) — transparent. IR spectrum (KBr, ν, cm^{-1}): 2960 s, 1360 m (CH_3), 2930 s, 1465 s, 735 s, 725 s (CH_2). Mass spectrum (100°C, 50 eV, 0.5 mA), *m/z* (I_{rel}, %): 338 (9), 324 (14), 310 (18), 296 (24), 282 (49), 268 (62), 254 (100), 240 (86), 226 (74) (M^+).

Aromatic hydrocarbons (arylalkenes) were eluted by hexane. White grease-like substance, R_f 0.84 (system 5). Red-violet spot on treatment with 50% H_2SO_4 (110°C). IR spectrum (film, ν, cm^{-1}): 785, v.s. UV spectrum (hexane, λ_{max}, nm): 229. Mass spectrum (120°C, 40 eV, 0.5 mA), *m/z* (I_{rel}, %): 326 (5), 312 (6), 298 (6), 284 (8), 270 (20), 256 (28), 242 (39), 228 (56) (M^+), 134 (48), 133 (89), 119 (100), 105 (96), 91 (81), 79 (55).

FA esters were eluted with hexane. The fractions included sterol esters (R_f 0.85) and triterpenol esters (R_f 0.82, system 6). Red-violet spot on treatment with 50% H_2SO_4 (110°C).

Mass spectrum of the ester fraction (100°C, 40 eV, 0.5 mA), *m/z* (I_{rel}, %): $M^+ \cdot M^+$: 690 (1.5), 688 (1.5), 664 (0.5), 678 (2.0), 676 (1.8), 664 (0.8), 662 (3.8), 652 (0.9), 650 (0.3), 648 (0.4), 638 (1.3), 624 (0.7); fragment ions: 396 (100), 394 (50), 382 (32), 368 (18), 273 (74), 267 (30), 265 (25), 263 (8), 255 (89), 239 (28), 218 (69), 213 (58), 203 (75), 189 (83).

The products of severe alkaline hydrolysis were FAs and free sterols and triterpenols.

The esters of FAs with a low-molecular-mass alcohol, triacylglycerols, free FAs, alkanols, triterpenols, sterols, 1,2- and 2,3-diacylglycerols, and monoacylglycerols had the physicochemical indices described in the literature [18, 19].

The qualitative and quantitaive evaluation of the tanning substances and flavonoids was carried out by the standard methods of [20].

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