Chemistry of Natural Compounds, Vol. 32, No. 1, 1996

LIPIDS OF THE PROCESSING WASTES FROM SOME MEDICINAL PLANTS

T. V. Khomova, S. D. Gusakova, and A. I. Glushenkova

UDC 547.915:665.1/3

The lipid and fatty acid compositions of the wastes arising in the production of drugs from Aralia mandshurica, Digitalis lanata, Glaucia flavum, Ephedra equisetina, *and* Ferula varia *have been studied.*

Continuing a study of the lipids of the wastes from the production of plant medicinal preparations [1, 2], we have investigated the compositions of the five samples of wastes from the processing of medicinal plants given in Table 1.

We have shown previously that, depending on the species, the plant organ, and the technology used for its processing, the lipids may be concentrated in the resinous (1), liquid (2), or solid (3) wastes. In view of this, the specimens for the present investigation were taken from various technological stages (see Table 1) in which the concentration of lipids in the wastes was possible.

It can be seen from Table 1 that the yields of extractive substances from medicinal plant wastes vary within wide limits, and in the case of the treatment of *D. lanata* leaves and the epigeal parts of *G. flavum* and *F. varia* may reach 97-98% of the weight of the waste. The yield of resinous waste on the weight of the initial raw material was 4-5% for *D. lanata*, 3-4% for *G. flavum*, and 2.5-3.7% for *F. varia*.

The qualitative compositions of the lipids of the extracts isolated were established by analytical TLC in systems used for the chromatography of neutral lipids (NLs) and phospho- and glycolipids (PLs and GLs) [1, 2], using aliquots of the extracts. It was found that all the extracts, with the exception of the eluate from Al_2O_3 in the case of *D. lanata*, consisted of NLs, PLs, and GLs.

The following classes of compounds were detected in the *D. lanata* resin and in the wastes from *F. varia* and *A. mandshurica*: hydrocarbons, carotenoids, wax esters, esters of sterols and of triterpenols and lower alcohols (possibly ethanol and/or methanol) with fatty acids, free sterols and triterpenols, triacylglycerols (TAGs), free fatty acids (FFAs), fatty alcohols, hydroxylipids, and transformed chlorophylls and xanthophylls.

Of the above-mentioned components, TAGs, fatty acids, and triterpenols were absent from the wastes of *G. flavum*, and, as was to be expected, the pigments of photosynthetic tissues (chlorophylls, carotenoids, and xanthophylls) were not found in the wastes from *A. mandshurica* roots. FFAs predominated quantitatively in the NLs of all the samples.

The phospholipids of extracts of the wastes studied had poorer qualitative compositions than those of the initial plant biomasses [6, p. 261]. The numbers of components that we detected in them ranged from one (phosphatidic acid in the *D. lanata* resin and in the *A. mandshurica* meal) to four (phosphatidylcholine, phosphatidylinositol, lyso-phosphatidylcholine, and phosphatidic acid in *E. equisetina*).

The glycolipids of all the samples, excluding the eluate from Al_2O_3 that had been used in the production of tselanid from *D. lanata*, were represented by mono- and digalactosyldiacylglycerols and sterol glycosides and their esters; in addition, the *D. lanata* resin and the *E. equiseta* meal contained one, and the *A. mandshurica, G. flavum*, and *F. varia* wastes two, unidentified compounds including a sugar residue. Thus, regardless of the technology used for processing medicinal plants, the most labile class of polar lipids was the PLs and the least mobile was the GLs. No marked differences were detected in the composition of the GLs in dependence on the method of technological processing, the species, and the plant organ.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (3712) 89 14 75. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 19-23, January-February, 1996. Original article submitted October 23, 1995.

 0009-3130/96/3201-0014$15.00

TABLE 1. Characteristics of Samples of the Medicinal Plant Processing Wastes that were Studied

Drug raw material	Desired product	Technological stage concentrating lipids	Yield of the waste	Yield of lipids and lipophilic substances, % on the weight of the waste
1. *Aralia mandshurica* Rupr. et Maxim., fam. Araliaceae, roots	Sarapal [3, p. 186]	Extraction of the aralosides from the plant raw material with methanol	Meal	0.94
2. *Digitalis lanata* Ehrh., fam. Scrophulariaceae, leaves	Celanide [3, p. 150]	a) Evaporation of methanolic extracts	Resin	97.0
		b) Purification on Al_2O_3	Spent Al_2O_3	0.09
3. *Glaucium flavum*, fam. Papaveraceae, epigeal part	Glaucine hydrochloride [3, p. 111, 135]	a) Evaporation of acetone extracts	Acetone mother liquor	98.0
		b) Purification on Al_2O_3	Spent Al_2O_3	0.87
4. *Ephedra equisetina* Bunge, fam. Ephedraceae, epigeal part	Ephedrine hydrochloride [3, p. 120]	Extraction of alkaloids from the raw material	Meal	6.8
5. *Ferula varia*, fam. Umbelliferae, epigeal part	Cynaroside [4]	Treatment of an alcoholic filtrate with chloroform	Chloroform mother solution	98.0

TABLE 2. Amounts of Fatty Acids and Sterols in the Wastes from the Processing of Medicinal Plants

Plant species and waste	Amount, mg/g of lipids		
	sterols	total fatty acids	FFAs
Aralia mandshurica	22.8	78.9	28.6
Digitalis lanata (resin)	16.7	339.3	59.7
Glaucium flavum			
a) Acetone mother liquor	7.3	326.5	97.9
b) Al_2O_3	Tr.	329.3	99.8
Ephedra equisetina	9.9	353.4	78.3
Ferula varia	22.9	270.7	52.0

The eluate from Al_2O_3 in the processing of *D. lanata* contained no PLs. In it we identified only components of the NLs, namely: wax esters, FFAs, alkanols, sterols, terpenols, and xanthophylls. In addition, when the concentrated eluate was subjected to TLC on silica gel in the chloroform–methanol–NH_4OH (65:5:4) system we established the presence of appreciable amounts of five components with R_f 0.40, 0.67, 0.76, 0.87, and 0.93 giving on treatment with the Dragendorff reagent the orange coloration that is characteristic for nitrogen bases. Since these compounds did not simultaneously give a blue coloration on treatment with the Vas'kovskii reagent, and, consequently, did not belong among the PLs, their further identification was not pursued.

A quantitative estimation was made of the main components of the NLs — the sterols and FFAs — that had been isolated from the initial extracts by preparative TLC (Table 2). The total FAs were obtained from portions of the extracts by saponification under severe conditions [6, p. 87] and they were determined gravimetrically.

In view of the smallness of the amount of substances in the eluate from the *D. lanata* Al_2O_3, these indices were not determined for them.

It can be seen from Table 2 that the proportion of FFAs in the samples investigated was 3-10% (28.6-99.8 mg/g) of the weight of the extract. The amount of total FAs was 3-6 times greater than that of FFAs. This shows that the acids of the lipids of the wastes investigated were present mainly in bound form.

The sterols content (Table 2) ranged from 0.7 to 2.3% on the weight of the extracts. According to their mass spectra, the sterol-triterpenol fractions of all the samples consisted of β-sitosterol, stigmasterol, campesterol, and cholesterol and the two triterpenols cycloartanol and cycloartenol [1, 2]. Of the above-mentioned components, no cholesterol was found in the wastes from the processing of *F. varia*.

The compositions of the fatty acids of the total lipids and of the FFAs were determined by the GLC and mass spectroscopy of their methyl esters (Table 3). High levels (up to 70% of the weight of the acids) of the 18:2 and 18:3 acids were found in all the samples, while in the acetone mother solution from *G. flavum* the 18:2 acid alone made up more than 55% of the weight of the acids. The lipids of all the medicinal plant processing wastes studied also contained trace amounts of acids of the C_{20} series, and in the lipids of *E. equisetina* all the saturated acids from C_{20} to C_{30} were detected, their total amount exceeding 10%.

It can be seen from Table 3 that the *F. varia* and *D. lanata* wastes were enriched with the 18:3 acid. Moreover flavonoids with a possible antioxidant effect [7] were found in these wastes. In order to check the degree of resistance to oxidation of the lipids of the *F. varia* wastes on storage, we determined the qualitative composition of the lipids and their total fatty acid composition after these wastes had been stored at 22-24°C for 12 months. The results showed that on prolonged storage of the resinous wastes obtained by evaporating the chloroform mother solution there were practically no changes in the qualitative composition of the lipids and no oxidative-destructive changes in the fatty acids.

Thus, by generalizing the results given in this paper and those published previously [1, 2] it may be concluded that, regardless of the species and the organ of the plant undergoing processing and also of the nature of the medicinal preparation being isolated from it, the lipid and lipophilic compounds are concentrated in the form of resinous wastes at the stage of treating with a less polar solvent than the primary crude extract obtained with a polar extractant.

EXPERIMENTAL

The conditions for recording the mass spectra and for GLC and TLC, and the methods of identifying the lipid classes and of isolating and identifying the FAs have been described in [1, 2].

TABLE 3. Compositions of the Fatty Acids of the Lipids from Medicinal Plant Processing Wastes, % GLC

Acid	*A. mandshurica*		*D. lanata*		*G. flavum*			*E. equisetina*		*F. varia*		
	total	FFAs	total	FFAs	acetone mother solution		Al_2O_3 Al_2O_3 total	total	FFAs	total		FFAs
					total	FFAs				1	2	
X_1	1.1	0.6	–	–	0.2	Tr.	0.2	0.1	0.7	0.2	0.2	0.2
X_2	–	–	–	–	–	–	–	Tr.	0.4	–	–	–
10:0	0.5	0.4	0.4	–	0.2	Tr.	0.2	0.2	0.6	0.2	0.2	0.1
11:0	0.4	0.5	Tr.	–	Tr.	–	Tr.	2.3	5.4	–	–	–
12:0	0.7	0.9	0.4	0.2	0.4	Tr.	0.7	0.6	0.9	0.5	0.6	Tr.
13:0	0.6	0.2	Tr.	–	Tr.	–	Tr.	0.1	0.4	Tr.	Tr.	–
14:0	1.4	1.4	1.8	0.7	0.8	Tr.	1.7	0.9	0.9	0.9	0.8	0.9
14:1	Tr.	Tr.	–	–	0.6	Tr.	0.8	0.7	Tr.	0.5	0.6	Tr.
14:3	0.8	0.3	–	–	–	–	Tr.	0.3	Tr.	0.7	Tr.	Tr.
15:0	1.3	0.7	Tr.	–	0.7	Tr.	0.9	1.1	0.2	0.7	0.9	0.6
16:0	46.1	27.5	35.6	39.8	5.5	5.6	18.8	17.8	36.8	27.7	26.0	38.3
16:1	1.7	1.4	0.7	1.0	1.9	1.0	1.0	2.0	1.9	2.0	1.9	1.4
16:3	Tr.	0.6	Tr.	0.4	1.9	Tr.	1.0	0.8	0.3	Tr.	0.8	0.2
16:4	Tr.	0.4	–	–	Tr.	Tr.	1.1	0.4	Tr.	–	–	–
17:0	Tr.	Tr.	–	–	Tr.	Tr.	Tr.	Tr.	Tr.	6.1	7.7	4.9
18:0	4.1	6.5	0.5	1.7	1.9	Tr.	3.4	5.8	3.3	2.8	2.1	2.2
18:1	12.7	13.7	0.8	2.8	14.2	16.9	13.9	15.2	10.2	4.5	3.2	2.7
18:2	24.9	29.1	20.9	25.8	55.2	65.2	32.8	19.8	20.1	25.8	24.9	23.8
X_3	Tr.	5.6	–	–	–	–	–	–	–	–	–	–
18:3	Tr.	2.8	38.9	27.6	16.5	11.3	23.5	25.7	17.9	27.5	30.1	24.7
20:0	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	Tr.	0.7	Tr.	Tr.	Tr.	Tr.
21:0	Tr.	Tr.	Tr.	–	Tr.	–	Tr.	0.9	–	Tr.	Tr.	–
22:0	3.7	3.6	Tr.	–	Tr.	–	Tr.	3.3	–	Tr.	Tr.	–
23:0	Tr.	Tr.	Tr.	–	Tr.	–	Tr.	Tr.	–	Tr.	Tr.	–
24:0	Tr.	3.8	Tr.	–	Tr.	–	Tr.	1.3	–	Tr.	Tr.	–
25:0	–	–	Tr.	–	Tr.	–	Tr.	Tr.	–	Tr.	Tr.	–
26:0	–	–	Tr.	–	–	–	Tr.	Tr.	–	Tr.	Tr.	–
27:0–30:0	–	–	–	–	–	–	–	Tr.	–	–	–	–

*1) Unstored waste; 2) waste stored for a year.

Samples of the wastes after the production of tsinarosid from *F. varia* were supplied by A. U. Mamatkhanov of the Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, and the other samples of wastes were obtained from the Chimkent pharmaceutical chemicals factory. The resinous wastes and the liquid wastes after evaporation were dissolved in chloroform. The lipids were isolated from meals by Folch's method [6, p. 74] and those from spent Al_2O_3 were eluted with chloroform.

The preparative TLC of the lipids was conducted on silica gel L 5/40 (Czechoslovakia) with the addition of 1% of $CaSO_4$ in the hexane–diethyl ether (1:1) system.

REFERENCES

1. T. V. Khomova, S. D. Gusakova, and A. I. Glushenkova, Khim. Prir. Soedin., 37 (1995).
2. T. V. Khomova, S. D. Gusakova, and A. I. Glushenkova, Khim. Prir. Soedin., 210 (1995).
3. V. P. Zakharov, N. I. Libizov, and Kh. A. Aslanov, Drugs from Plants and Methods for their Production [in Russian], Fan, Tashkent (1980), p. 232.
4. É. Kh. Batirov, M. P. Yuldashev, G. A. Nezhinskaya, and V. M. Malikov, Khim. Prir. Soedin., 727 (1979).
5. T. V. Khomova and S. D. Gusakova, Maslo-zhir. Prom-st', No. 10, 30 (1981).
6. M. Kates, Techniques of Lipidology, American Elsevier, New York (1972) [Russian translation, Mir, Moscow (1975), p. 323].
7. Ref. Zh. Khim., No. 21 (1992), part III, Abstract R1259.