THE COMPOSITION OF THE ORGANIC ACIDS OF CO_2 EXTRACTS OF SOME SPICE-AROMATIC PLANTS

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UDC 547.917

It has been shown previously that essential oils contain free or bound acids, and some extractive oils of spice-aromatic plants containing both free organic acids and their triglycerides. There is information on a high fatty-acid content in a numer of spice and essential-oil crops [1-3]. Usually, organic acids are isolated from a complex mixture with an aqueous solution of sodium carbonate or caustic soda and acid components of esters of nonglyceride nature by saponification with a weak solution of sodium carbonate [4].

The volatile aliphatic acids from C_1 to C_6 are separated in the form of their ammonium salts by paper chromatography, and also in the form of various derivatives (hydrazides and hydroxamates) and with the aid of partition or ion-exchange column chromatography [5]. The GLC separation of volatile acids has become particularly widely used in the last few years [6-8]. The acids are separated in the free form and in the form of esters (methyl). It is recommended that the higher fatty acids (C_8-C_{20}) should be separated in the form of salts or in the form of methyl esters [9].

The present paper gives the results of an investigation of the component composition of the organic acids isolated from CO_2 extracts of spice-aromatic plants (the fruit of *Piper nigrum*, family Piperaceae, *Capsicum annuum* L., family Solanaceae, and *Vitex agnuscastus* L., family Verbenaceae, the leaves of *Cinnamomum sieboldi* M., family Lauraceae, and the rhizomes of *Curcuma domestica* Val., family Zingiberaceae, and of *Armoracia rusticana*, family Cruciferae).

The fractions of steam-volatile free acids and of the acids of esters of nonglyceride nature were found to contain the low-molecular-weight saturated acids of the alipatic series from C_1 to C_7.

The main acids of the black pepper extract proved to be acetic (57.3%) and enanthic (19.5%) (Table 1). Esters of the aliphatic series from C_1 to C_6 were found, and of these the valeric acid ester amounted to 23.1% and the caproic acid ester to 70.8% (Table 2). The fractions of the volatile matter in the extract of the lilac chaste-tree were similar in composition to the acids of the black pepper fraction, the main component being enanthic acid (40.6%). In the ginger extract the compositions of the volatile acids and of the esters were similar, the main acids being formic, propionic, valeric, and enanthic, and the esters those of acetic (58%), butyric (10%), and caproic (10.4%) acids (see Table 2).

TABLE 1. Compositions of the Steam-Volatile Free Acids Isolated from CO_2 Spice Extracts (%, GLC)

Acid	Index	Ginger	Cinnamon	Curcuma	Black pepper	Red pepper	Lilac chaste-tree	Horse-radish
Formic	C_1	30,4	6,8	28,6	4,8	11,3	18,2	23.1
Acetic	C_2	6,5	3,4	3,6	57,3	20,3	16,8	61,7
Propionic	C_3	14,4	20,6	18,6	2,2	17,5	12,4	3,8
Butyric	C_4	5,3	4,6	2,8	1,3	8,2	0,8	1,5
Isovaleric	C_5-iso	7,1	36,6	5,4	6,0	3,1	4,0	1,3
Valeric	C_5	14,6	10,4	16,6	1,1	5,8	0,6	1,6
Caproic	C_6	5,4	—	3,8	7,8	5,0	6,6	4,0
Enanthoic	C_7	16,3	17,6	20,6	19,5	28,8	40,6	1,6
Unidentified	—	—	—	—	—	—	—	1,4

Krasnodar Scientific-Research Institute of the Food Industry. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 763-767, November-December, 1977. Original article submitted May 12, 1977.

0009-3130/77/1306-0643$07.50

TABLE 2. Compositions of the Ester-Bound Acids of Nonglyceride Nature of CO_2 Spice Extracts (%, GLC)

Acid	Index	Ginger	Cinnamon	Curcuma	Black pepper	Red pepper	Lilac chaste-tree	Horseradish
Formic	C_1	—	10,5	—	1,5	13,5	6,8	2,0
Acetic	C_2	58,0	6,8	36,4	3,8	42,6	4,5	64,3
Propionic	C_3	7,8	18,6	10,6	0,8	—	1,2	7,8
Butyric	C_4	10,0	3,4	4,8	—	4,0	10,4	3,0
Isovaleric	C_5-iso	7,6	—	11,0	—	—	—	9,0
Valeric	C_5	6,2	36,4	18,8	23,1	31,3	36,5	2,5
Caproic	C_6	10,4	24,3	18,4	70,8	8,6	40,6	11,4

The higher (bound) fatty acids in the extract were represented in the form of triglycerides. The acids from C_{10} to C_{18} were found in the black pepper extract, the main ones being capric, palmitoleic, palmitic, and stearic. The triglycerides of the lilac chaste-tree extract were similar in composition.

EXPERIMENTAL

The compositions of the organic acids of the extracts were investigated mainly by the GLC method. The complex mixture of acids was analyzed on the basis of the previous isolation of groups according to their physicochemical properties: the steam-volatile acids, the acids obtained after hydrolysis of the esters, and the fatty acids bound in the form of triglycerides.

Isolation of the Steam-Volatile Acids. The free organic acids were isolated from the extract by vigorously stirring it with 2% aqueous sodium bicarbonate for 2 h. The sodium salts of the acids were freed from residues of the extracts by repeated extraction with diethyl ether.

The volatile acids were distilled off with steam after acidification of the sodium carbonate solution. The distillate was titrated with alkali (0.1 N KOH) and was then evaporated to dryness on the water bath. The qualitative composition was determined by reaction gas chromatography based on the instantaneous reaction between the salts of the acids and potassium ethyl sulfate

$$RCOOK + C_2H_5SO_4K = RCOOC_2H_5 + K_2SO_4,$$

by L. G. Astakhova's method [10].

Isolation of the Ester-Bound Acids. The acids of esters of nonglyceride nature were isolated from the extracts by treatment with 5% aqueous NaOH. The unsaponified fraction was separated from the saponified fraction by extraction with diethyl ether and it was then acidified to a weakly acid reaction in order to destroy the sodium salts of the phenols and the acid components of the esters. The latter were extracted with diethyl ether and the extract was shaken with 2% aqueous sodium bicarbonate solution. They were freed from phenols by elution with petroleum ether. The aqueous solution of the sodium salts was acidified with 10% HCl and distilled with steam. The fraction of the volatile acids from the esters was isolated by the method described above. The qualitative composition of the volatile acids and the acids obtained after the hydrolysis of the esters were determined by the GLC method.

Conditions for GLC: DIP-1 chromatograph, flame-ionization detector, stainless-steel column 200 × 0.4 cm packed with Celite 545, 60-80 mesh, with a liquid phase consisting of a mixture of 25% diethylene glycol adipate—2% phosphoric acid—3% boric acid at 110°C and a rate of flow of the carrier gas (nitrogen) of 40 ml/min.

The components of the acid fraction were identified by the retention times of pure "markers" and a curve was plotted of the dependence of the logarithm of the retention on the number of carbon atoms in the molecule of the acid. The quantitative calculation of each component was performed by the internal-standard method. The results of the analysis are shown in Tables 1 and 2.

TABLE 3. Composition of the Fatty Acids of the Triglycerides of CO_2 Spice Extracts (%, GLC)

Acid	Index	Ginger	Cinnamon	Curcuma	Black pepper	Lilac chaste-tree	Horseradish
Enanthic	C_7	—	4,0	—	—	—	—
Caprylic	C_8	—	16,4	—	—	—	—
Pelargonic	C_9	17,6	24,5	20,9	—	—	—
Capric	C_{10}	14,0	12,4	14,4	22,5	20,5	—
Undecanoic	$C_{11:0}$	11,6	—	10,6	7,8	6,4	—
Lauric	$C_{12:0}$	16,2	12,6	9,4	5,1	3,7	6,4
Tridecanoic	C_{13}	7,3	—	6,7	2,8	2,4	—
Myristic	$C_{14:0}$	—	12,6	—	3,3	14,5	7,5
Myristoleic	$C_{14:1}$	—	3,9	—	—	0,5	—
Pentadecanoic	$C_{15:0}$	—	—	—	2,3	—	—
Unidentified	—	—	—	—	—	1,0	—
Palmitoleic	$C_{16:1}$	24,1	8,6	30,0	23,2	20,4	25,6
Palmitic	$C_{16:0}$	9,2	5,0	8,0	10,5	10,6	2,0
Unidentified	—	—	—	—	—	—	—
Stearic	$C_{18:0}$	—	—	—	22,5	20,0	5,6
Oleic	$C_{18:1}$	—	—	—	—	—	18,6
Linoleic	$C_{18:2}$	—	—	—	—	—	28,1
Linolenic	$C_{18:3}$	—	—	—	—	—	6,2

Isolation of the Nonvolatile Fatty Acids. The nonvolatile ether-soluble fatty acids from the residue of the saponified fraction of the extract were dissolved in petroleum ether (40-60°C) and were extracted by the passage of the solution through Amberlite IRA-400 resin in the hydroxyl form. The adsorbed acids were converted into the methyl esters directly on the resin. For this purpose, 30 ml of absolute methanol containing 10% HCl was poured onto the resin and the mixture was stirred by a magnetic stirrer for 20 min. The resulting solution was filtered off and transferred to a separating funnel, and the methyl esters were extracted with a mixture consisting of 15 ml of water and 60 ml of petroleum ether.

The composition of the nonvolatile fatty acids in the form of esters was analyzed by the GLC method.

GLC conditions: DIP-1 chromatograph with flame-ionization detector; separation using a stainless-steel column 300 × 0.4 cm containing 20% of ethylene glycol succinate on Chromosorb (60-80 mesh), 160°C, rate of flow of the carrier gas (nitrogen) 40 ml/min. The results of the analysis are given in Table 3.

SUMMARY

1. It is desirable to analyze the composition of the organic acids of CO_2 spice extracts after their preliminary separation into individual groups according to their physicochemical properties: steam-volatile, ester-bound obtained after the hydrolysis of esters of nonglyceride nature, and acids forming components of the triglycerides.

2. Characteristic for the fraction of steam-volatile free acids and for the ester-bound acids in the CO_2 extracts obtained after the hydrolysis of esters of nonglyceride nature are the C_1-C_7 low-molecular-weight saturated acids of the alipatic series: formic, isovaleric, valeric, caproic, etc. The higher fatty acids present include acids with even and odd numbers of carbon atoms from C_8 to C_{18} and also acids with saturated and unsaturated bonds.

3. The compositions of the lower acids in the extracts of all the samples studied are qualitatively very similar. Their quantitative compositions differ fundamentally. At the same time, differences both in the qualitative and in the quantitative compositions of the glyceride acids of the samples investigated are more pronounced. This is due to the circumstance that fruit was subjected to extraction in one case and leaves and rhizomes in another.

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THE STRUCTURES OF THE BROMOHYDROXYOCTADECANOATES FORMED IN THE REACTIONS OF THE DIASTEREOMERIC METHYL ESTERS OF DIEPOXYOCTADECANOIC ACIDS WITH HYDROGEN BROMIDE

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UDC 547.396+547.710

In view of the fact that a report has recently appeared in the literature on dibromo- and tetrabromooctadecanoic acids isolated from the oil of the seeds of *Eremostachys moluccelloides* [1], it is a matter of undoubted interest to investigate the structure of the corresponding synthetic bromine-containing analogs that are formed by the reaction of diepoxyoctadecanoic acids with hydrogen bromide. This reaction forms the basis of a method for determining epoxide oxygen that is widely used in the chemical, foodstuffs, and oils and fats industries [2]. But in the case of the methyl ethers of threo- and erythro-cis-9,10:cis-12,13-diepoxyoctadecanoic acids (I and II, respectively) (diastereomeric diepoxides of methyl linoleate) [3], this method leads to a rather low percentage of epoxide oxygen, particularly for the erythro isomer (II). Thus, for the threo isomer the percentage of epoxide oxygen comes to 9.52 and for the erythro isomer 9.04 (the calculated value being 9.80). A similar anomaly has been pointed out in the literature [4]. A lowering of the results of the determination of epoxide oxygen has also been observed for diepoxides of terpenes [5], but the cause of this phenomenon has not so far been explained.

The present paper gives the results of a study of a number of bromohydroxy compounds obtained by the reaction of the diastereomeric methyl esters (ME's) of cis-9,10:cis-12,13-diepoxyoctadecanoic acids with hydrogen bromide. The investigation of the reaction products, performed under various conditions, has shown that in all cases identical compounds are formed: together with the isomeric open-chain products of addition of two molecules of the reagent — dibromodihydroxyoctadecanoates — cyclic derivatives — substituted tetrahydrofurans and tetrahydropyrans — are formed as the result of the addition of one molecule of HBr (Table 1).

The reaction of the threo isomer (I) with hydrogen bromide gave a complex mixture of substances (Scheme 1) from which by preparative chromatography on silica gel we isolated: the ME of threo-10-bromo-9-hydroxy-(threo-10-bromo-12-bromo)-threo-12-bromo-13-hydroxyoctadecanoic acid (III) (yield 4-9%, R_f 0.52, mp 45-46°C from hexane containing ether); the ME of threo-9-bromo-10-hydroxy-(threo-10-hydroxy-12-hydroxy)-threo-13-bromo-12-hydroxyoctadecanoic acid (IV) (yield 44-52%, R_f 0.68, mp 92-92.5°C from ethanol); fraction A (yield 20-25%, R_f 0.57, mp 30-32°C (from hexane) — a mixture of the ME's of threo-9-bromo-10-hydroxy-(erythro-12-bromo-10-hydroxy)-threo-12-bromo-13-hydroxy- and threo-10-bromo-9-hydroxy-(erythro-10-bromo-

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A. A. Zhdanov Leningrad State University. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 767-776, November-December, 1977. Original article submitted June 23, 1977.

0009-3130/77/1306-0646$07.50