

ARTICLES

## Determination of the Composition of Volatiles in Cognac (Brandy) by Headspace Gas Chromatography–Mass Spectrometry

A. G. Panosyan\*, G. V. Mamikonyan\*, M. Torosyan\*, E. S. Gabrielyan\*, S. A. Mkhitaryan\*\*, M. R. Tirakyan\*\*, and A. Ovanesyan\*\*

\*Gyul'bekyan Laboratory of Drug Quality Control, Agency on Drugs and Medicinal Technologies of the Armenian Ministry of Public Health, ul. Komitasa 49/4, Yerevan, 375051 Armenia

\*\*Yerevan Cognac plant of the Pernod Ricard group, prosp. Isakova 2, 375082 Armenia

Received November 22, 2000; in final form, January 31, 2001

**Abstract**—A method for the quantitative determination of easily volatile compounds in cognac (brandy) by headspace gas chromatography–mass spectrometry was developed. Alcohols and carboxylic acid aldehydes, acetals, and ethylates were identified by comparing their mass spectra with those presented in the Wiley database, and by comparing their relative retention times with those of reference materials of the known composition. Detection limits for test compounds ranged from 0.02 to 0.2 mg/L. Statistically valid difference in the concentration of compounds with different aromas or specific odors was demonstrated for cognacs aged for 3, 10, and 20 years. The concentration of cognac-flavored compounds, such as diethylacetal and carboxylic acid esters, for example, ethyl formate, significantly increased with age, whereas the concentration of alcohols (butanols, allyl alcohol, hexenol, and toxic methanol) considerably decreased. Comparison analyses of some Armenian, Moldavian, Georgian, Ukrainian, Russian, Kyrgyz, and French cognacs were carried out.

The analysis of cognac (brandy) by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) usually involves the extraction of low-molecular compounds with nonpolar solvents from a matrix containing lignans and tannins [1–10]. The extraction step may be considered a drawback of the procedures, because every step of sample pretreatment introduces additional errors into the final results, extends the time of analysis, and raises its cost. In this work, headspace analysis, which is now most commonly used in investigations of different kinds of wine [11–17], was extended to cognacs. A vial with a cognac sample was heated to certain temperature. Volatile components formed the vapor phase, which was automatically injected in a capillary column for the separation of components, their identification, and quantification by the external standard method.

### EXPERIMENTAL

A Hewlett Packard HP 6987 gas chromatographic–mass spectrometric system was used in our work. The system involved an HP 6890 plus gas chromatograph equipped with an HP 5973 mass spectrometric selective detector, an HP 7694 headspace sampler, and an HP MSD Chemstation (HP Vectra VE) system with an HP Laser Jet 1100 printer for data acquisition and processing.

A fused-silica capillary column (60 m long, 0.25 mm i.d.) with a 0.50  $\mu\text{m}$ -film of HP-INNOWAX

stationary phase (Hewlett-Packard 19091N-236, cross-linked polyethylene glycol) was used.

Cognac samples were chromatographed in a helium flow (1.3 mL/min). The temperature program began at 35°C (1 min), was raised at a rate of 5 K/min to 238°C and was held for 5 min.

Portions (4 mL) of cognac (brandy) were sampled with a measuring pipette and placed in a 20-mL vial, which was tightly stoppered and set in a holder of the HP 7694 gas-phase sampler.

A single injection of samples was performed under the following conditions: column thermostat temperature of 70°C; temperature of the transfer line, 120°C; sample equilibration time, 10 min; the time of filling the sample loop, 12 s; the loop equilibration time, 3 s; and the time of sample injection, 1 min.

The components of test mixtures were quantified from calibration graphs built in the same concentration ranges as test compounds occurred in cognacs (from 1 to 5000 mg/L). The reference compounds and concentration ranges of calibration mixtures are listed in Table 1.

Mass spectra were obtained using the ionization of sample molecules with electron impact (electron beam 70 eV). The total ion current (TIC), which was interrupted as ethanol left the column, was detected. The data were acquired from the total ion spectra. For the quantification of analytes, mass spectra were recorded in the selected-ion monitoring (SIM) mode to enhance the selectivity of the analysis.

**Table 1.** Reference substances and concentration ranges of calibration mixtures

Reference substance	Concentration, mg/L
Ethyl formate	1–10
Ethyl butyrate	1–10
Ethyl hexanoate (ethyl caproate)	1–10
Ethyl octanoate (ethyl caprilate)	1–10
Ethyl decanoate (ethyl caprate)	1–10
Ethyl dodecanoate (ethyl laurate)	1–10
Ethyl tetradecanoate (ethyl myristate)	1–10
Ethyl hexanoate (ethyl palmitate)	1–10
Isoamyl dodecanoate	1–10
3Z-Hexenol-1	1–10
2-Propenol-1 (allyl alcohol)	1–10
Butanol-1	1–10
Butanol-2	1–10
Acetylmethylcarbinol (acetoin)	1–10
Isoamyl acetate	1–10
Propenal-2 (acrolein)	1–10
3-Methylbutanal (isovaleraldehyde)	1–10
$\gamma$ -Butyrolactone	1–10
Isobutanal	1–10
Furfural	1–20
Diethyl succinate	1–20
Ethanal (acetaldehyde)	10–100
Hexanol-1	10–100
Acetal (diethylacetal of acetaldehyde)	10–100
2-Phenylethanol	10–100
Propanol-1	50–500
2-Methylbutanol-1	50–500
2-Methylpropanol-1 (isobutanol)	50–500
Ethyl acetate	50–500
Ethyl lactate	50–500
3-Methylbutanol (isoamyl alcohol)	500–5000
Methanol	100–2000

For each compound under examination, several most specific ions were selected to avoid the effect of other components with close retention times.

All components were detected at the same dwell time ( $D_{well}$ ). The quantitative results for test samples were obtained automatically on the completion of the analysis. The substances were quantitatively deter-

mined by measuring the intensities of the target and confirming ions and the ratios between them. The data on the target and confirming ions of 29 volatile compounds in cognac and on their retention times are summarized in Table 2.

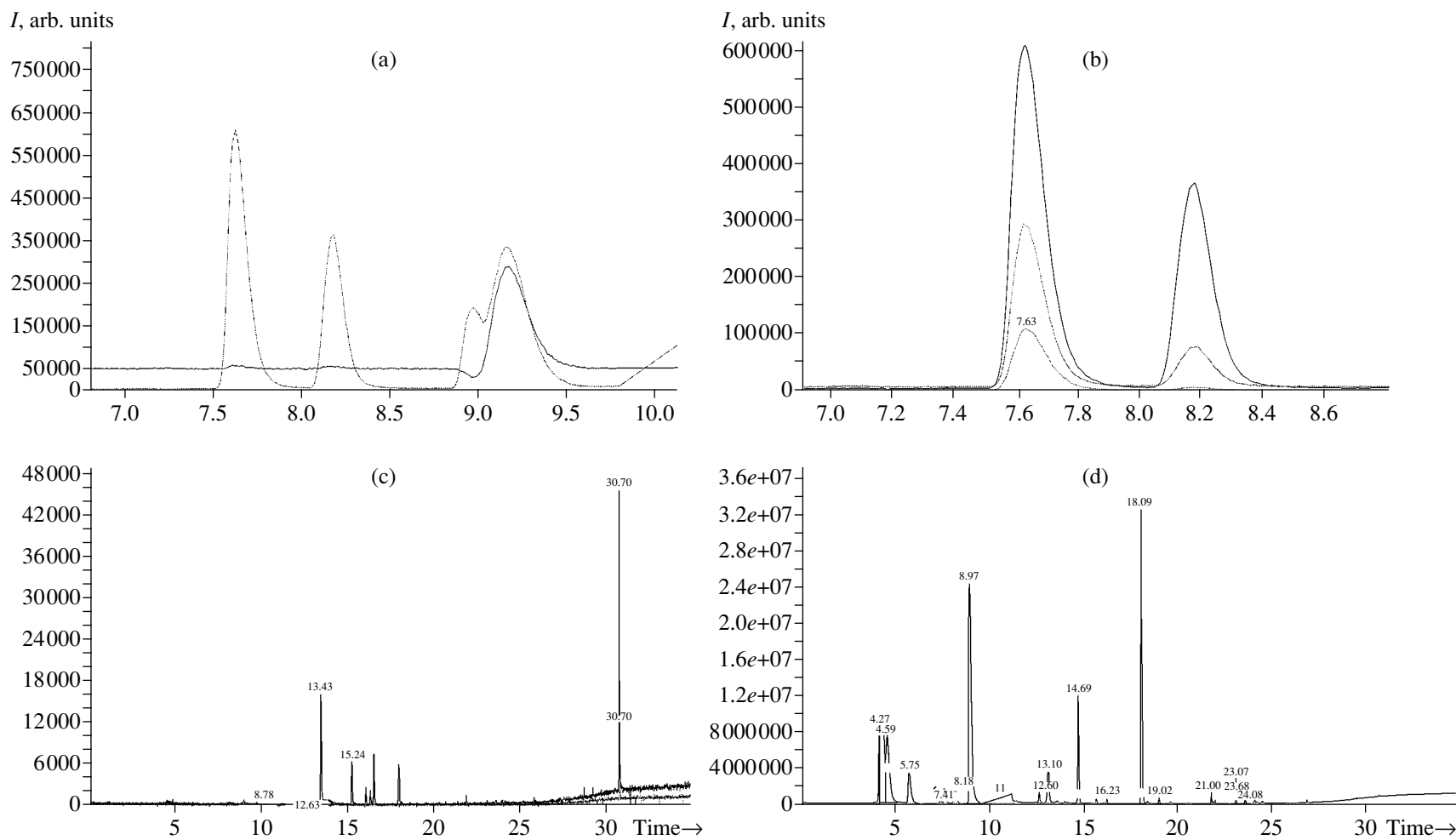
The data were statistically processed by an unpaired two-sided *t*-test with a confidence probability of 95%. Average values were calculated using PRISM Statistical Software Version 2.01, 1996.

## RESULTS AND DISCUSSION

Figure 1 presents chromatograms of cognac volatile compounds detected by the signals of selected ions. Every compound was identified using the HP Wiley 275 and NIST98 MS (Hewlett-Packard, 1998) databases.

The procedure used for the quantitative analysis of model solutions containing 10 mg/L of each of the typical cognac volatiles demonstrated that these substances can be determined at this concentration with an acceptable error, which, in the majority of cases, was no higher than 30 rel. % (Table 3). The data presented in Table 4 showed that five successive cycles of headspace extraction under the above-mentioned conditions left the set of the analyzed cognac volatile compounds virtually unchanged. Similar results were obtained for typical fermentation products (allyl, propyl, isomeric butyl, and pentyl alcohols). The method exhibited high accuracy and was characterized by a variation coefficient of lower than 5% for almost all test compounds. The described method was used for the analysis of cognacs from different batches aged for 3, 10, and 20 years.

A statistically valid difference in the concentration of compounds with different aromas or specific odors was demonstrated for cognacs aged for 3, 10, and 20 years. The concentration of cognac-flavored compounds such as diethylacetal and carboxylic acid esters, for example, ethyl formate, significantly increased with age (Fig. 2), whereas the concentration of alcohols (butanols, allyl alcohol, hexenol, and toxic methanol) considerably decreased (Fig. 3). At the same time, the concentration of a number of other compounds remained virtually unchanged during the aging of cognacs. All these changes that took place on the long storage of cognac (during its aging) may be explained by the nonenzymatic oxidation of alcohols and aldehydes to acids, followed by their esterification in ethanol with the formation of ethylates and acetals from aldehydes. For example, an increase in the concentration of ethyl formate and diethylacetal may be due to the oxidation of methanol to formaldehyde and then to formic acid, which, in their turn, in the presence of



**Fig. 1.** Chromatograms of (a) methanol ( $m/z$  31, 32), (b) ethyl formate ( $m/z$  31, 45, 74), and (c) 2-phenylethanol ( $m/z$  91, 122) recorded in selected-ion monitoring mode; and (d) total ion chromatogram of volatile compounds of cognac Nairi.

**Table 2.** Retention times and masses of calibrating ions (target/confirming) of cognac volatiles ( $D_{\text{well}} = 100$  ms)

Substance*	Retention time, min	Calibrating ions: target/confirming
Acetaldehyde (ethanal)	5.75	44/43
Diethylacetal of acetaldehyde	8.99	45/73; 103
Diethylacetal of formaldehyde	8.18	103/59; 31
Isobutanal	7.39	43/41; 72
Ethyl acetate	8.97	43/88; 61
Methanol	9.16	32/31
Ethyl formate	7.63	31/45; 74
Ethyl butyrate	13.10	71/88; 43
Butanol-2	12.64	45/59
Butanol-1	16.21	56/41; 43; 31
Propanol-1	13.07	31/59; 60
Methyl-2-propanol-1	14.70	43/41; 74
Methyl-2-butanol-1	18.05	57/56; 70; 41
Methyl-3-butanol-1	18.05	55/56, 57, 70, 41
Allyl alcohol	15.35	57/39
Hexanol-1	21.77	56/69
3Z-Hexenol-1	22.54	67/41; 82
Acrolein	8.1	55/56
Ethyl hexanoate	19.00	88/99
Ethyl octanoate	23.57	88/101; 127
Ethyl decanoate	26.85	88/101; 155; 157
Ethyl dodecanoate	29.47	88/100; 157; 185
Ethyl lactate	21.77	45/75
Diethyl succinate	27.45	101/129; 45
Isoamyl acetate	15.65	43/70; 55
Isoamyl decanoate	29.7	70/155
2-Phenylethanol	30.69	91/122
Acetoin	20.75	45/44; 88
Furfural	24.46	96/95

\* The obtained mass spectra differed from those presented in the library by 1–3%.

**Table 3.** Accuracy of the method (concentration of substances was 10 mg/L)

Substance	Found (average of 5 replicates), mg/L	Coefficient of variation, %	Substance	Found (average of 5 replicates), mg/L	Coefficient of variation, %
Methyl-2-propanol-1	12.91	21.99	Acrolein	4.17	1.674
Ethyl formate	0.83	2.828	Ethyl hexanoate	8.85	18.74
Ethyl butyrate	8.48	14.27	Ethyl octanoate	11.69	39.11
Butanol-2	10.04	9.093	Ethyl decanoate	10.64	35.45
Butanol-1	9.24	6.493	Ethyl dodecanoate	13.04	53.84
Allyl alcohol	9.34	5.958	Isoamyl acetate	8.28	53.84
Hexanol-1	1.85	1.686	Isoamyl decanoate	12.13	45.07
3Z-Hexenol-1	8.34	1.674	Acetoin	7.15	30.77

**Table 4.** Analysis of cognac volatile components by the successive injection of headspace samples

Substance	Retention time, min	Found after sample injection					Average, mg/L	Standard deviation of average	Standard deviation	Coefficient of variation, %
		No 1	No 2	No 3	No 4	No 5				
Acetaldehyde (ethanal)	5.75	109.55	113.01	121.55	117.82	116.67	115.72	2.058	4.60	3.97
Diethylacetal of acetaldehyde	8.99	68.25	69.01	71.85	70.22	70.04	69.87	0.61	1.36	1.95
Diethylacetal of formaldehyde	8.18	0.98	1.00	0.68	0.81	0.68	0.83	0.07	0.16	19.28
Isobutanal	7.39	10.79	11.00	11.67	11.28	11.12	11.17	0.15	0.33	2.95
Ethyl acetate	8.97	504.77	510.78	530.63	519.04	521.96	517.44	4.48	10.02	1.94
Methanol	9.16	158.16	159.14	153.53	145.52	143.72	152.01	3.18	7.10	4.67
Ethyl formate	7.63	19.46	20.08	21.64	21.13	20.90	20.64	0.39	0.87	4.21
Ethyl butyrate	13.10	6.99	7.27	7.61	7.50	7.49	7.37	0.11	0.25	3.39
Butanol-2	12.64	74.32	76.09	76.41	74.31	73.21	74.87	0.60	1.34	1.79
Butanol-1	16.21	116.20	120.41	116.57	113.39	114.84	116.28	1.17	2.63	2.26
Propanol-1	13.07	342.62	347.22	339.68	327.06	327.10	336.74	4.12	9.21	2.73
Methyl-2-propanol-1	14.70	523.96	536.53	531.51	519.20	526.54	527.55	3.00	6.71	1.27
Methyl-2-butanol-1	18.05	868.18	893.14	878.12	858.71	860.45	871.72	6.36	14.22	1.63
Methyl-3-butanol-1	18.05	1867.88	1950.88	1879.07	1837.83	1823.01	1871.75	22.20	49.64	2.65
Allyl alcohol	15.35	17.86	18.32	17.88	17.34	17.67	17.81	0.16	0.36	2.02
Hexanol-1	21.77	25.47	27.81	26.01	25.16	25.85	26.06	0.46	1.03	3.95
3Z-Hexenol-1	22.54	1.37	1.01	0.82	0.79	0.77	0.95	0.11	0.25	26.31
Acrolein	8.1	1.63	2.23	1.44	1.43	1.42	1.63	0.15	0.35	21.47
Ethyl hexanoate	19.00	4.49	4.63	4.76	4.68	4.71	4.65	0.05	0.10	2.15
Ethyl octanoate	23.57	11.27	12.13	12.14	12.14	12.26	11.99	0.18	0.40	3.34
Ethyl decanoate	26.85	13.49	14.49	14.16	14.66	14.72	14.30	0.23	0.50	3.49
Ethyl dodecanoate	29.47	17.01	16.23	15.34	14.02	13.36	15.19	0.68	1.51	9.94
Diethyl succinate	27.45	5.48	7.99	7.53	7.19	6.89	7.02	0.43	0.954	13.59
Isoamyl acetate	15.65	2.75	2.81	2.97	2.90	2.92	2.87	0.04	0.09	3.13
Isoamyl decanoate	29.7	16.41	16.08	14.70	4.62	4.58	11.28	2.74	6.13	54.34
2-Phenylethanol	30.69	25.45	26.74	33.89	41.01	44.32	34.28	3.75	8.38	24.44
Acetoin	20.75	9.89	9.71	9.28	9.61	9.10	9.518	0.14	0.32	3.36
Furfural	24.46	9.88	10.22	9.53	9.24	9.21	9.62	0.19	0.43	4.47

**Table 5.** Concentration of volatiles (mg/L) in different cognacs (years of cognac ageing are given in parentheses)

Substance	Armenian cognac KS, sample 1 (10)	Armenian cognac KS, sample 2 (20)	French cognac Napoleon, sample 1	French cognac Napoleon, sample 2	Ukrainian cognac KS (15)	Georgian cognac KS (10–12)	Russian cognac KVVK (8–10)	Kyrgyz cognac KV (6–7)	Dagestan cognac KS (25)	Karabakh cognac KVVK, sample 1 (9)	Karabakh cognac KS, sample 2 (10)
Acetaldehyde (ethanal)	188.32**	216.37**	88.54	110.22	138.48	58.65	69.45	69.45	138.68	92.01	137.92
Diethylacetal of acetaldehyde	111.01	129.58	34.23	40.39	76.41	25.87	33.24	33.24	75.02	51.00	71.41
Diethylacetal of formaldehyde	8.60	15.82	3.31	5.82	2.49	-0.07	0.94	0.94	6.22	0.30	4.69
Isobutanal	9.37	5.51	4.86	7.49	4.88	2.73	5.21	5.21	5.06	1.76	3.01
Ethyl acetate	649.23	738.80	196.00	204.79	458.29	168.19	219.10	219.10	515.65	294.46	451.32
Methanol	163.87	49.25	82.77	40.85	55.18	105.17	108.18	108.18	53.68	66.38	175.44
Ethyl formate	52.68	65.36	23.60	33.40	22.25	12.02	15.46	15.46	37.22	12.81	34.70
Ethyl butyrate	10.50	12.26	1.29	1.13	3.97	0.65	-0.10	-0.10	12.72	3.08	2.61
Butanol-2	26.22	32.79	4.78	2.52	9.93	21.47	12.87	12.87	45.05	20.60	15.61
Butanol-1	23.750	27.35	2.47	1.94	9.22	8.54	7.60	7.60	15.85	10.73	11.31
Propanol-1	331.30	343.11	145.37	117.83	165.42	169.97	195.46	195.46	163.38	261.79	153.85
Methyl-2-propanol-1	457.01	542.61	534.04	464.42	249.22	405.31	340.47	340.47	367.29	241.44	271.21
Methyl-2-butanol-1	646.59	767.85	461.78	455.22	373.44	449.76	387.81	387.81	442.09	339.49	386.71
Methyl-3-butanol-1	1334.57	1809.36	657.22	637.09	211.59	485.96	257.60	257.60	442.08	103.51	196.96
Allyl alcohol	5.31	5.50	1.38	0.34	1.45	2.17	1.31	1.31	13.90	3.76	1.43
Hexanol-1	14.11	16.21	12.07	10.32	11.02	15.99	15.46	15.46	10.11	16.16	9.29
3Z-Hexenol-1	0.38	0.23	2.18	1.63	0.38	0.74	0.60	0.60	0.19	0.41	0.42
Acrolein	1.50	1.44	1.43	1.44	1.42	1.42	1.45	1.45	1.43	1.43	1.43
Ethyl hexanoate	2.55	3.19	2.48	2.20	2.84	1.08	1.69	1.69	2.34	2.02	1.49
Ethyl octanoate	5.41	6.66	16.82	10.08	7.23	6.69	8.55	8.55	6.68	6.68	4.89
Ethyl decanoate	4.36	6.03	21.26	5.86	7.13	8.11	6.47	6.47	6.39	4.64	5.06
Ethyl dodecanoate	7.42	6.60	12.08	7.23	2.69	11.37	8.88	8.88	9.99	9.26	9.78
Diethyl succinate	4.52	5.30	2.85	0.93	2.82	2.41	1.61	1.61	3.96	2.69	2.68
Isoamyl acetate	1.92	3.29	0.46	0.45	0.89	0.49	0.46	0.46	1.45	0.65	0.92
Isoamyl decanoate	4.88	4.72	4.50	4.93	5.14	4.52	4.79	4.79	5.19	4.69	4.96
2-Phenylethanol	84.08	79.08	76.88	55.45	61.97	74.77	56.29	56.29	57.57	59.88	58.22
Acetoin	8.34	8.44	3.59	1.76	5.01	2.99	2.63	2.63	5.35	2.97	3.81
Furfural	13.12	13.36	11.86	9.73	6.40	10.33	14.78	14.78	7.56	4.89	4.73

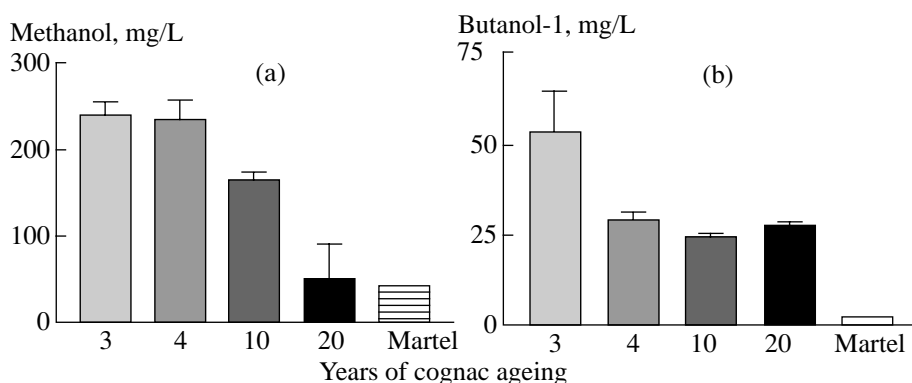


Fig. 2. Changes in concentrations of (a) methanol and (b) butanol-1 in cognacs as functions of cognac age (years of cognac ageing are plotted on the abscissa not to scale).

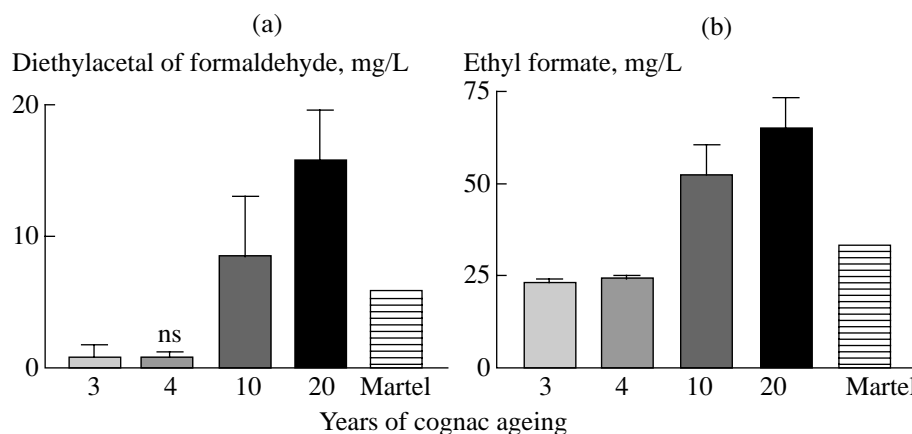
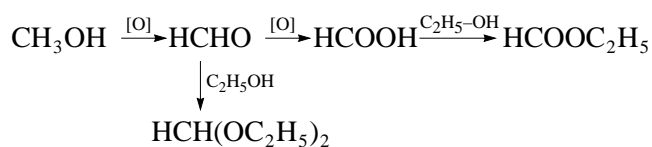


Fig. 3. Changes in concentrations of (a) diethylacetal of formaldehyde and (b) ethyl formate in cognacs as functions of cognac age (years of cognac ageing are plotted on the abscissa not to scale).

excess ethanol, is converted to diethylacetal and ethyl formate, respectively.



A low concentration of methanol in old cognacs confirmed this assumption. An increase in the concentrations of isoamyl acetate and ethyl acetate during the aging of cognacs may be explained by the esterification of isoamyl and ethyl alcohols with acetic acid, respectively. Among aldehydes, only the concentration of butanal increased on cognac storage. In other words, long storage and aging certainly improved the chemical composition of cognacs, reducing the concentration of “bad” and increasing the concentration of “good” volatile ingredients that characterize its flavor.

It should be also noted that the concentration of volatile compounds in different batches of fine cognacs (variation coefficient) turned to be more uniform than the concentration of these substances in different batches of ordinary three-star cognac. Table 5 presents

the results of analyses of cognacs of different origin, namely, Armenian, Moldavian, Georgian, Ukrainian, Russian, Kyrgyz, and French cognacs. These data demonstrate that there is no clearly pronounced, statistically significant difference in the composition of easily volatile compounds in different cognacs. Thus, the developed method can be proposed for the rapid determination of easily volatile components of cognac and brandy in quality-control laboratories.

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