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Received for review July 17, 1978. Accepted October 23, 1978. Reference to a company and/or product named by the Department is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

Composition of Neutral Volatile Constituents in Grape Brandies

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The neutral volatile constituents in different grape brandies (French and German grape brandies, French cognacs) have been investigated by gas chromatography and coupled gas chromatography-mass spectrometry. Using standard controlled aroma separation by liquid-liquid extraction, prefractionation on silica gel, and identification by mass spectrometry, 139 neutral volatile compounds were quantitatively determined by gas chromatography. Clear quantitative differences exist between the amounts of some aroma constituents of German and French grape brandies as well as French cognacs. The mean values and ranges of the individual components are given for the three groups of grape brandies. The quantitative differences within the groups caused by different technologies of grape brandy production are discussed.

Wine as well as grape brandies may be considered as final links of a biotechnological sequence (Drawert, 1974). In the case of brandy this sequence is extended by distillation and aging. These additional technological steps influence the quality of the products by appropriate distillation processes and aging conditions. In this connection, in the countries with traditional methods of distillation of wines into brandies, the distillation and aging processes are subjected to legal regulations. The national decrees are adapted to the common EC regulations (Bitzer, 1974). In principle, the aim of all the decrees is to require a sufficiently long holding time during distillation at high temperatures to limit the concentration of ethanol in order to obtain adequate amounts of volatile compounds in the distillate.

Little is known about the raw materials of German grape brandies investigated in this work. For the distillates a minimum storage time of 6 months in oak casks is prescribed. Products declared as "old" grape brandies require a minimum storage time of 12 months. No minimum storage time is required for French grape brandies. These products can also be manufactured in Germany by diluting the imported refined distillate (Bitzer, 1974). Only grape brandies produced according to the strong regulations of the "appellation contrôlée jaune d'or" are permitted to be declared cognacs. The French law requires minimum storage time of 1 year for cognacs declared "trois étoiles". For all the other declarations a minimum storage time of 4 years must be regarded.

The qualitative composition of aroma compounds has been reviewed in several papers (Schaefer and Timmer,

1970; Rapp, 1972; Marché and Joseph, 1975; Yoshizawa, 1975). Apart from some exceptions (Litschew, 1976), the quantitative investigations have related to the main components such as esters (Koch et al., 1971; Reinhard, 1972; Hieke and Sage, 1973; Braun and Hieke, 1974; Postel et al., 1975; Heß and Trott, 1977) and fusel alcohols (Webb et al., 1952; Reinhard, 1970; Drawert et al., 1967; Woidich and Pfannhauser, 1974; Connell and Strauss, 1974; Postel et al., 1975). The qualitative and quantitative composition of neutral volatile constituents isolated from different grape brandies is presented in this paper.

EXPERIMENTAL SECTION

Samples. Each of eight commercial samples of French and German grape brandies as well as French cognacs (VSOP) were investigated.

Liquid-Liquid Extraction. Each of 700 mL of grape brandy (diluted with 1300 mL of H₂O) was used adding three internal standards before the extraction: 420 µg/L of methyl octanoate, 440 µg/L of dimethyl methylmalonate, and 680 µg/L of 2-methyl-1-pentanol. The volatiles were isolated by liquid-liquid extraction for 8 h using pentane. A 100-mL organic phase was used for 1 L of diluted brandy (Drawert and Rapp, 1968). The aroma extracts were concentrated to 3 mL in a Vigreux column (45 °C) as described (Drawert et al., 1969). Commercial grade solvents (99%), further purified by redistillation, were used for liquid-liquid extraction.

Column Chromatography on Silica Gel. Aroma extracts (3 mL) were fractionated on silica gel 60 (Merck), activity grade II, using a pentane-diethyl ether solvent system (Schreier and Drawert, 1976; Schreier et al., 1978). Glass columns 1.8 i.d. × 40 cm containing 48 g of silica gel maintained at 11-13 °C were used. The elution rate was 60 mL/h and three fractions were obtained. Fraction I was eluted with 300 mL of 10% diethyl ether in pentane (internal standard methyl octanoate). Fraction II was eluted with 300 mL of 20% diethyl ether in pentane

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Table I. Calibration Factors (Including Liquid-Liquid Extraction, Preseparation on Silica Gel, and Gas Chromatography)

compound	silica gel fraction	factor (F_g)	compound	silica gel fraction	factor (F_g)
isopentyl acetate	I	2.22 ± 0.18	diisopentyl succinate	II	0.82 ± 0.09
pentyl acetate	I	2.20 ± 0.20	diethyl glutarate	II	0.72 ± 0.08
hexyl acetate	I	1.65 ± 0.15	1-pentanol	III	1.04 ± 0.08
<i>cis</i> -3-hexenyl acetate	I	0.82 ± 0.10	2-pentanol	III	0.95 ± 0.11
2-phenethyl acetate	I	0.62 ± 0.08	3-pentanol	III	0.92 ± 0.12
isopentyl propanoate	I	1.28 ± 0.12	3-methyl-1-pentanol	III	1.02 ± 0.07
ethyl 3-ethoxypropanoate	II	1.04 ± 0.12	4-methyl-1-pentanol	III	1.04 ± 0.09
isobutyl 2-hydroxypropanoate	III	0.64 ± 0.08	1-hexanol	III	1.01 ± 0.10
isopentyl 2-hydroxypropanoate	III	0.68 ± 0.07	<i>cis</i> -3-hexen-1-ol	III	0.66 ± 0.08
hexyl 2-hydroxypropanoate	III	0.66 ± 0.07	<i>trans</i> -2-hexen-1-ol	III	0.61 ± 0.08
ethyl butanoate	I	1.93 ± 0.18	2-ethyl-1-hexanol	III	0.92 ± 0.08
isobutyl butanoate	I	1.82 ± 0.18	1-heptanol	III	1.20 ± 0.10
isopentyl butanoate	I	1.71 ± 0.18	2-heptanol	III	0.92 ± 0.09
2-phenethyl butanoate	I	0.54 ± 0.07	1-octanol	III	1.25 ± 0.10
ethyl 2-methylbutanoate	I	2.20 ± 0.18	2-octanol	III	0.82 ± 0.09
isobutyl 2-methylbutanoate	I	2.25 ± 0.20	<i>trans</i> -2-octenol	III	0.61 ± 0.08
isopentyl 2-methylbutanoate	I	2.00 ± 0.19	1-octen-3-ol	II	0.65 ± 0.08
ethyl 3-methylbutanoate	I	2.12 ± 0.20	1-nonanol	III	1.16 ± 0.12
isopentyl 3-methylbutanoate	I	1.85 ± 0.22	2-nonanol	III	0.92 ± 0.08
ethyl pentanoate	I	1.60 ± 0.15	1-decanol	III	0.84 ± 0.09
isopentyl pentanoate	I	1.20 ± 0.10	benzylalcohol	III	1.20 ± 0.15
ethyl hexanoate	I	1.58 ± 0.12	2-phenylethanol	III	1.15 ± 0.10
isobutyl hexanoate	I	0.88 ± 0.09	linalool	II	2.51 ± 0.18
isopentyl hexanoate	I	0.86 ± 0.08	4-terpinenol	II	2.22 ± 0.19
2-phenethyl hexanoate	I	0.52 ± 0.06	1,1-diethoxy-2-methylpropane	I	1.45 ± 0.12
ethyl <i>trans</i> -2-hexenoate	I	0.50 ± 0.06	1,1-diethoxypropan-2-one	II	0.82 ± 0.10
ethyl <i>cis</i> -3-hexenoate	I	0.62 ± 0.06	1,1-diethoxy-3-methylbutane	I	1.28 ± 0.11
ethyl heptanoate	I	0.80 ± 0.07	1,1-diethoxy-pentane	I	1.20 ± 0.11
isobutyl heptanoate	I	0.82 ± 0.07	1,1-diethoxyhexane	I	1.02 ± 0.11
ethyl octanoate	I	0.67 ± 0.06	1,1-diethoxyphenylethane	I	0.82 ± 0.09
isobutyl octanoate	I	0.68 ± 0.06	1,1-diisopentoxyethane	I	0.62 ± 0.08
isopentyl octanoate	I	0.64 ± 0.07	benzaldehyde	I	1.48 ± 0.16
ethyl 3-hydroxyoctanoate	III	1.01 ± 0.12	thiophene-2-carboxaldehyde	II	0.68 ± 0.08
ethyl nonanoate	I	0.81 ± 0.07	2-methylcyclopentanone	II	0.88 ± 0.09
isobutyl nonanoate	I	0.88 ± 0.09	furyl methyl ketone	II	0.72 ± 0.09
methyl decanoate	I	0.90 ± 0.11	acetophenone	II	0.92 ± 0.10
ethyl decanoate	I	0.82 ± 0.09	damascenone	I	0.42 ± 0.05
isobutyl decanoate	I	0.88 ± 0.10	linalool oxides	III	1.21 ± 0.10
isopentyl decanoate	I	0.66 ± 0.08	4-ethylphenol	II	0.23 ± 0.03
ethyl dodecanoate	I	0.62 ± 0.05	γ -octalactone	III	0.62 ± 0.07
isopentyl dodecanoate	I	0.66 ± 0.05	<i>cis</i> - β -methyl- γ -octalactone	III	0.52 ± 0.06
ethyl 2-furanoate	I	0.42 ± 0.05	<i>trans</i> - β -methyl- γ -octalactone	III	0.55 ± 0.06
ethyl phenylacetate	I	0.69 ± 0.07	γ -nonalactone	III	0.50 ± 0.06
diethyl oxalate	II	0.25 ± 0.03	γ -decalactone	III	0.42 ± 0.05
diethyl succinate	II	0.62 ± 0.07			

(internal standard dimethyl methylmalonate), and fraction III was obtained eluting with 250 mL of diethyl ether (internal standard 2-methyl-1-pentanol).

All eluates were concentrated to 0.5 mL before further examination.

Gas-Liquid Chromatography. The separation and quantification of individual components was done using a Varian Aerograph Model 2701 (A) and a Siemens gas chromatograph Model L 400 (B), both equipped with flame ionization detectors. A was fitted with a glass column, 5 m × 2 mm i.d., packed with 5% FFAP on Varaport 30 (80–100 mesh) (C1). B was equipped with a glass column, 3.5 m × 2 mm i.d., packed with 5% UCON LB 550 X on Varaport 30 (80–100 mesh) (C2). The operation conditions were as follows: injection port temperature, 220 °C (A, B); detector temperature, 280 °C (A) and 220 °C (B); column temperatures were programmed from 70–175 °C at 2 °C/min, 175–250 °C at 6 °C/min (C1), and 70–200 °C at 2 °C/min (C2). Carrier gas (N₂) flow, 20 mL/min; hydrogen flow, 30 mL/min; air flow, 300 mL/min (A, B).

Using internal and external standards, quantitative determinations were carried out by measuring peak heights. Calibration factors which account for individual components differences in liquid-liquid extraction, pre-fractionation on silica gel, and gas chromatographical analysis were employed (Table I). The determination of

these factors (F_g) has previously been described in detail (Schreier et al., 1978). The calculations were carried out according to the following equations:

$$m_1 = \frac{H_{1Si}m_{1St}}{H_{1St}F_g} \quad (1)$$

$$m_2 = \frac{H_{2Si}m_{2St}}{H_{2St}F_g} \quad (2)$$

Hence

$$F_g = \frac{(H_{2Si}m_{2St}/H_{2St}) - (H_{1Si}m_{1St}/H_{1St})}{m_2 - m_1}$$

where m_1 = naturally occurring amount of aroma constituent without addition of test substance ($\mu\text{g/L}$), m_2 = total amount of aroma constituent after addition of test substance ($\mu\text{g/L}$), H_{1Si} = peak height of aroma compound without addition of test substance (cm), H_{2Si} = peak height of aroma compound after addition of test substance (cm), H_{1St} = peak height of standard in experiment without addition of test substance (cm), H_{2St} = peak height of standard in experiment with addition of test substance (cm), m_{1St} = amount of added standard in experiment without addition of test substance ($\mu\text{g/L}$), m_{2St} = amount of added standard in experiment with addition of test

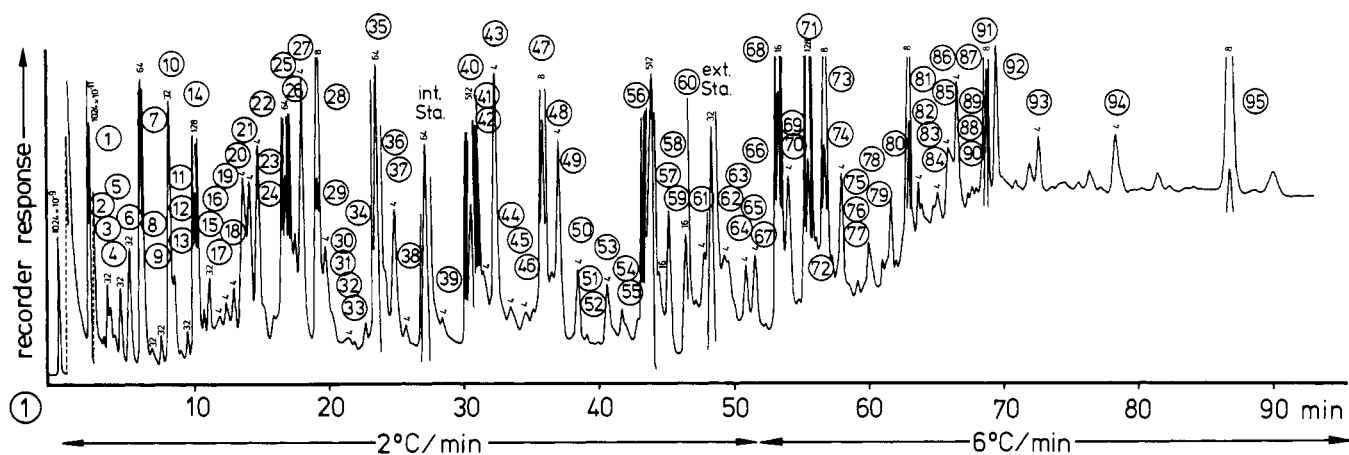


Figure 1. Gas chromatographic separations of volatile compounds in a French grape brandy (silica gel fractions 1-3). Column C1: injections, 1 μ L. Further conditions are given in the Experimental Section. Int. Sta = internal standards (see Experimental Section); ext. Sta = external standards, butyl nonanoate (fraction 1), γ -heptalactone (fractions 2 and 3). The peak numbers correspond to the numbers in Table II.

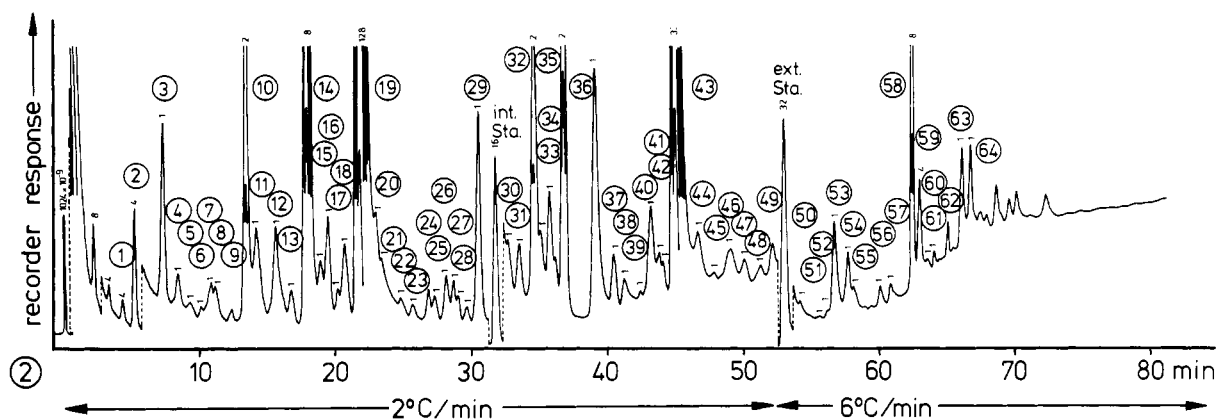


Figure 2. See caption to Figure 1.

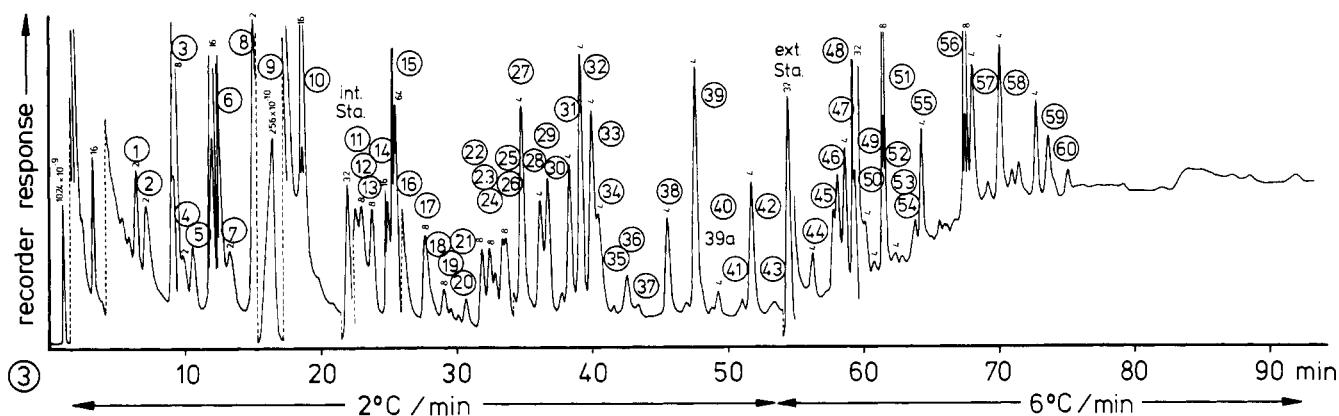


Figure 3. See caption to Figure 1.

substance (μ g/L), F_g = total calibration factor corresponding to the internal standard substances. As it can be seen from Table I, the standard deviations were found between ± 5 and $\pm 15\%$.

Gas Chromatography-Mass Spectrometry. A Varian Aerograph Model 1201 coupled via a Watson-Bieman helium separator to a mass spectrometer CH 7 (Varian-MAT, Bremen) was used. The gas chromatograph was fitted with two types of columns. C3: 60 m \times 0.5 mm i.d. stainless steel SCOT column coated with Carbowax 20 M (Perkin-Elmer) was used for the separation and identification of volatiles from the fractions I and II (helium flow, 2.9 mL/min). For the components of fraction III, a "Micropak" glass column 5 m \times 1 mm i.d., packed with 5% FFAP on Varaport 30 (100-120 mesh) (C4) was used;

helium flow, 4.1 mL/min. C3 and C4 were operated at a temperature programmed from 70-100 $^{\circ}$ C at 1 $^{\circ}$ C/min, 100-200 $^{\circ}$ C (C3) and 100-240 $^{\circ}$ C (C4) at 2 $^{\circ}$ C/min. Injection volumes were 0.1 μ L (C3) and 0.5 μ L (C4). The ion source temperature was 250 $^{\circ}$ C. Mass spectra, recorded on a Siemens oscillograph, were obtained at 70 eV.

RESULTS AND DISCUSSION

The results of the qualitative and quantitative investigations of volatile compounds in grape brandies are summarized in Table II. The gas chromatographic separations of the individual components in the three silica gel fractions are demonstrated by the example of a French grape brandy (Figures 1-3). Considering the aroma substances of the different chemical classes in relation to

Table II. Occurrence and Amounts of Volatile Compounds in Grape Brandies

esters	compound	peak no. ^a	identified and fraction	amounts, $\mu\text{g/L}$					
				German grape brandies		French grape brandies		Cognacs	
				m^h	r^h	m	r	m	r
	ethyl acetate ^d	1	I	336	78-1000	244	160-291	249	160-412
	isobutyl acetate ^c	6	I	2127	970-4955	1423	650-2272	1479	844-2732
	isopentyl acetate	14	I		<1-20		<1-13		<1-5
	pentyl acetate	19	I		35-75	59	18-111	89	21-207
	hexyl acetate	28	I	53	<1-3		<1-3		<1-23
	<i>cis</i> -3-hexenyl acetate ^{*g}	33	I		120-950	258	46-604	245	75-521
	2-phenylethyl acetate	68	I	327	6-101		<1-15		<1-22
	ethoxyethyl acetate ^{* + 2-octanone^c}	17	II	21	14-25	16	12-21	30	7-76
	diethoxyethyl acetate ^{c,*}	31	II	19	170-1182	440	160-794	267	93-575
	ethyl propanoate ^c	3	I	583	<1-19	24	9-47	10	5-37
	isopentyl propanoate	21	I	23	4-46	9	2-15	73	12-239
	ethyl 3-ethoxypropanoate [*]	20	II		<1-18	33	3-156		<1-3
	ethyl 2-oxopropanoate ^c	15	II		119-1463	1426	251-2257	2212	1076-4560
	ethyl 2-hydroxypropanoate ^c	14	III	816	<1-136	87	44-124	176	38-432
	isobutyl 2-hydroxypropanoate	24	III		21-778	392	100-727	1273	600-3245
	isopentyl 2-hydroxypropanoate	33	III	418	3-135	15	6-39	57	36-118
	hexyl 2-hydroxypropanoate [*]	40	III	36	62-452	402	106-666	329	161-569
	ethyl 2-methylpropanoate + 1,1-dithoxypropane ^c	4	I	268					
	isopentyl 2-methylpropanoate + limonene ^{c,*}	22	I	13	7-26	47	8-151	15	5-25
	ethyl 3-methylthiopropoate ^{*.c}	50	I	12	3-25	21	7-30	29	19-43
	ethyl butanoate	7	I	1915	738-3244	1300	822-1828	1100	903-1995
	isobutyl butanoate	18	I	8	5-10	7	6-9	8	6-11
	isopentyl butanoate ^d	28	I						
	2-phenylethyl butanoate	78	I	9	4-16	8	4-15	23	9-38
	ethyl 2-methylbutanoate	8	I	76	30-132	123	6-248	61	26-105
	isobutyl 2-methylbutanoate ^d	20	I						
	isopentyl 2-methylbutanoate	30	I		<1-7		<1-5		<1-4
	ethyl 3-methylbutanoate	9	I	157	90-207	219	9-402	114	54-202
	isopentyl 3-methylbutanoate	32	I		<1-12		<1-7		<1
	ethyl 2-hydroxy-3-methylbutanoate ^{*.c}	27/21	II/III	53	3-113	53	14-128	102	69-200
	ethyl pentanoate	15	I	119	53-250	165	38-471		1-13
	isopentyl pentanoate [*]	38	I		<1-12		<1-7		<1
	ethyl 2-hydroxy-3-methylpentanoate ^{*.c}	33/30	II/III	171	9-174	190	<1-26	45	19-106
	ethyl 2-hydroxy-4-methylpentanoate ^{*.c}	31	III	1372	788-1763	1815	991-2344	2472	1637-2839
	ethyl hexanoate	25	I	14	4-39	49	<1-36	25	<1-5
	isobutyl hexanoate	37	I						
	isopentyl hexanoate	43	I	47	16-157	54	14-145	168	12-32
	2-phenylethyl hexanoate	87	I	79	36-118		40-65		99-329
	ethyl <i>trans</i> -2-hexenoate	36	I		<1-4		<1-12		<1-8
	ethyl <i>cis</i> -3-hexenoate [*]	31	I		<1		<1		<1
	ethyl heptanoate	35	I	1154	200-4598	798	23-2160	36	11-200
	isobutyl heptanoate	42	I		<1		<1		<1
	ethyl octanoate	40	I	5640	3087-7164	8460	6636-9770	11680	7570-13614

Table II (Continued)

compound	peak no. ^a	identified and determined in fraction	amounts, ^b µg/L					
			German grape brandies		French grape brandies		Cognacs	
			m ^h	r ^h	m	r	m	r
isobutyl octanoate	51	I	<1	<1	<1	<1	6	3-10
isobutyl octanoate	58	I	145	36-357	159	77-302	161	113-222
ethyl nonanoate	49	I	56	10-118	48	15-130		<1
isobutyl nonanoate	57	I		<1-12		<1		<1
methyl decanoate	53	I	20	8-38	26	5-40	20	18-31
ethyl decanoate	56	I	6859	3453-9575	9490	5483-13667	13141	10330-15257
isobutyl decanoate	65	I	10	3-16	17	12-35	15	13-20
isopentyl decanoate	73	I	77	29-164	66	38-101	93	64-113
ethyl 9-decanoate ^{*c}	59	I	78	56-115	193	104-327	100	53-148
ethyl undecanoate ^d	63	I						
ethyl dodecanoate	71	I	1341	804-1870	1419	951-2129	2352	1740-3075
isopentyl dodecanoate	82	I	27	16-40	22	10-28	47	34-83
ethyl tetradecanoate ^c	81	I	88	58-130	90	60-138	167	92-418
isopentyl tetradecanoate ^c	92	I	40	32-60	32	22-50	50	23-170
ethyl hexadecanoate ^c	91	I	80	21-149	55	27-132	62	20-154
ethyl octadecanoate ^d	95	I						
ethyl 2-furanoate [*]	54	I	23	3-41	19	10-25	87	55-118
ethyl phenylacetate [*]	66	I	24	7-40	20	20-38	24	13-33
diethyl oxalate [*]	30	II	17	2-36	19	13-36		<1-35
diethyl malonate [*] + 5-methylfurfural ^c	36	II	101	41-157	176	86-279	47	8-109
methyl ethylsuccinate ^{*c}	39	II		<1-28		<1-20		<1-5
diethyl succinate	43	II	10233	1976-24660	6436	3441-14157	9442	3288-11390
ethyl n-propylsuccinate ^{*c}	47	II	15	6-30	11	9-15	11	3-23
ethyl isobutylsuccinate ^{*c}	49	II	39	7-60	31	14-42	50	19-85
ethyl isopentylsuccinate ^{*c}	54	II	325	108-500	236	108-330	240	90-500
diisopentylsuccinate [*]	62	II	55	11-141	26	5-108	259	51-585
diethyl methylsuccinate ^{*c}	41	II	24	8-40		<1-22		<1-8
diethyl fumarate [*] + phenylacetaldehyde ^c	40	II		<1-114	50	30-84	61	19-112
methyl ethylglutarate ^{*c}	46	II	102	15-303	15	6-60	22	2-91
diethyl glutarate [*]	48	II	23	7-30	10	6-14	21	4-50
alcohols								
1-propanol ^c	2	III	22	2-40	17	3-43	44	8-108
2-methyl-1-propanol ^c	3	III	177	36-295	158	110-227	378	195-630
3-methylthio-1-propanol ^{*c}	39a	III						
1-butanol ^c	6	III	1180	329-2684	1015	396-1821	1336	433-3060
2-butanol ^c	1	III	58	28-88	43	23-66	57	28-115
Σ 2- and 3-methyl-1-butanol ^c	9	III	63720	54870-76759	60030	51430-65030	79590	66740-122380
1-pentanol	10	III	313	156-454	138	49-325	54	33-97
2-pentanol	5	III	34	10-62	28	16-80	35	12-48
3-pentanol [*]	4	III	21	9-31	20	10-48		<1-40
3-methyl-1-pentanol [*]	13	III	129	105-157	130	103-144	192	140-263
4-methyl-1-pentanol [*]	11	III		<1-90		<1-108		<1-60
1-hexanol	15	III	6765	1682-8133	6391	1871-8505	10104	7000-12321
cis-3-hexen-1-ol	17	III	274	61-576	418	82-662	1264	845-2021
trans-3-hexen-1-ol ^d	16	III						
trans-2-hexen-1-ol	18	III	45	25-94	94	32-141	59	70-122
2-ethyl-1-hexanol [*]	27	III	76	24-202	28	12-102	38	13-60

Table II (Continued)

compound	peak no. ^a	identified and fraction	amounts, ^b μg/L					
			German grape brandies		French grape brandies		Cognacs	
			m ^h	r ^h	m	r	m	r
1-heptanol	23	III	125	85-170	132	78-176	121	99-156
2-heptanol	12	III	138	89-208	157	69-189	500	246-685
1-octanol	32	III	171	76-265	190	129-254	668	515-1000
2-octanol	20	III	9	2-20		<1-10		<1-6
trans-2-octen-1-ol*	35	III		<1-8		<1-5		<1-14
1-octen-3-ol*	29	II	210	124-324	174	93-242	121	51-300
1-nonanol	38	III	53	20-78	41	31-62	49	30-53
2-nonanol	30	III		<1		<1		<1
1-decanol	42	III	71	20-105	88	65-123	243	180-318
benzyl alcohol	45	III	20	5-38	26	10-216	21	5-40
2-phenylethanol	48	III	1556	825-3690	4400	652-7425	7289	4280-13088
linalool	35	II	310	88-395	234	190-275	274	107-471
hotrienol* ^{d,e}	37	II	38	16-58	24	15-40	24	10-40
4-terpinenol*	58	II	854	374-1600	654	223-1360	1175	508-2214
nerolidol* ^c + 4-ethylguajacol	39	III	182	93-335	100	76-126	325	250-414
α-terpineol								
acetals								
1,1-diethoxyethane ^{c,d}	1	I	18	5-26	10	6-15	22	5-51
1,1,2-triethoxyethane* ^c	13	II	268	62-452	402	106-666	329	161-569
1,1-diethoxypropane + ethyl 2-methylpropanoate ^c	4	I						
1,1,3-triethoxypropane ^c	19	II	2022	1300-2542	4162	1349-11460	747	318-1495
1,1-diethoxy-2-methylpropane	5	I	336	79-984	265	100-430	1670	1242-2600
1,1-diethoxypropan-2-one* ^f	14	II	625	91-1398	159	9-718	923	273-1970
3,3-diethoxybutan-2-one ^f	14	II	98	32-218	467	15-1066	21	4-40
1,1-diethoxy-3-methylbutane	11	I	200	42-612	204	8-354	170	28-300
1,1-diethoxypentane*	16	I	30	5-68		<1-222	5	2-11
1,1-diethoxyhexane*	26	I	10	4-35	10	3-19	30	14-61
1,1-diethoxyphenylethane*	61	I	18	3-30	35	1-51	12	1-39
1-ethoxy-1-isopentoxyethane* ^c	13	I	8	4-12	8	3-10	15	11-20
1,1-diisopentoxyethane*	34	I	9	2-18		<1-6	38	32-51
2,4,5-trimethyl-1,3-dioxolane ^c	2	I	171	30-435	43	15-96	21	7-49
ethyl pyruvate diethylketal* ^c	28	II	17	2-52	38	6-76		<1
carbonyls								
benzaldehyde	47	I	267	182-544	202	146-447	270	219-434
phenylacetaldehyde* + diethyl fumarate ^c	40	II		<1-114	50	30-84	61	19-112
furfural ^c	25	III	210	8-426	71	21-125	625	213-1195
5-methylfurfural + diethyl malonate ^{c,*}	36	II	101	41-157	176	86-279	47	8-109
thiophene-2-carboxaldehyde	44	II	21	5-45	7	3-12	45	20-80
2-pentanone	1	II	151	50-274	64	25-138	58	12-145
2-hexanone	4	II	71	30-108	74	15-117	20	9-51
2-heptanone	10	II	276	85-628	83	19-180	73	17-153
2-nonanone	24	II	19	2-107		<1-28		<1-22
4-(2',3',6'-trimethylphenyl)but-3-en-2-one* ^{d,e}								
2-methyl-5-hepten-6-one	21	II		<1	15	<1	9	<1
2-methylcyclopentanone*	11	II	25	11-38	35	4-43	35	4-14
furyl methyl ketone*	32	II	60	8-177		5-144		22-68
acetophenone*	42	II		<1		<1		<1
damascenone	69	I	19	12-39	35	18-45	152	102-257

Table II (Continued)

compound	peak no. ^a	identified and fraction determined in	amounts, ^b μg/L					
			German grape brandies		French grape brandies		Cognacs	
			m ^h	r ^h	m	r	m	r
miscellaneous								
2,4,6-trimethyl-1,3,5-trioxan* ^c	10	I	74	9-140	123	20-260	20	167-302
limonene* + isopentyl-2-methylpropanoate	22	I	13	7-26	47	8-151	15	5-25
3,8,8-trimethyl-dihydronaphthalene ^d	63	I						
1-(2,3,6-trimethylphenyl)-3-ethoxy-1-butene ^{d,e}								
vitispirane ^{d,e}								
cis-linalool oxide*	22	III	124	70-182	95	78-128	182	141-242
trans-linalool oxide*	26	III	101	10-226	109	88-136	271	10-424
4-ethylphenol*	64	II	244	134-452	174	111-212	130	19-249
4-ethylguajacol + nerolidol* ^c	58	II	854	374-1600	654	223-1360	1175	508-2214
γ-hexalactone* ^d	39a	III						
γ-octalactone*	49	III	49	22-63	33	3-75	242	127-662
cis-β-methyl-γ-octalactone	47	III	47	15-111	30	10-70	247	57-478
trans-β-methyl-γ-octalactone	51	III	115	30-242	121	30-238	736	146-1779
γ-nonalactone*	55	III	100	7-185	147	13-210	67	23-100
γ-decalactone* ^d	57	III						

^a The peak numbers correspond to the numbers in Figures 1-3. ^b Determined by standard controlled gas chromatographical analysis (column C1) considering calibration factors (Table I). ^c Determination without calibration factors ($F = 1.00$). ^d Not to be reproducibly determined. ^e Only identified by means of mass spectrometrical data. ^f Determination with column C2. ^g (*) For the first time identified in grape brandies, controlled by literature published (Marché and Joseph, 1975). ^h m , mean values; r , ranges.

their concentrations in the various groups of grape brandies the following conclusions may be drawn.

The main part of *esters* is formed by ethyl esters among which the average concentrations of C₃-, C₅-, C₇-, and C₉-ethyl esters show a definite minimum in cognacs. This clear difference in the quantitative distribution of ethyl esters of odd-numbered acids between the various groups of grape brandies has not been described as yet. Concerning the ethyl esters of even-numbered fatty acids a reverse behavior is detectable. The average concentrations of C₆-C₁₄-even-numbered ethyl esters are two times higher in cognacs than in the two other groups of grape brandies. These elevated amounts, especially of ethyl caprylate, caprylate, and laurate, are probably caused by the differences in distillation methods. It is well known that cognac is distilled in simple direct-fired pot stills including two successive distillations of wine. The first distillate is run with the yeast cells in the wine being distilled (Lafon et al., 1964). The ethyl ester amounts can be used to analytically differentiate cognacs from other groups of grape brandies (Postel and Adam, 1976).

A special effect could be observed concerning the concentrations of isopentyl esters in cognacs. In comparison to the two other groups of grape brandies, in cognacs minimal amounts of esters of short-chain fatty acids (C₃-C₅) are estimated against maximal values of esters of long-chain acids (C₁₀-C₁₄). It may be presumed that the long first distillation of cognac liberates more hi-boilers esters from the yeast fat reserves than does continuous column distillation. Furthermore, an increase of concentrations of long-chain compounds due to the extended aging of cognacs cannot be excluded.

In comparison to the two other groups of grape brandies, cognacs show higher amounts of ethoxy and hydroxy esters. The high concentrations of ethoxy compounds should be related to the strong influence of temperature during the "Méthode Charentaise" and to the long aging process. The elevated contents of hydroxy esters, in particular of lactates, in cognacs seem to be caused by the natural fermentation conditions including malolactic fermentation.

Due to the relatively high polarity of short-chain *alcohols*, the determination of these components occurring in ppm ranges is rather difficult after extractive enrichment. It is more favorable to determine these compounds by other analytical methods, e.g., distillation. Thus, concerning this class of volatiles, calibration factors have not been determined ($F_g = 1.00$). A relative comparison exhibits elevated concentrations of 1-propanol and isopentanol in the group of cognacs, a fact already observed by Postel et al. (1975). Contrary to the results of these authors, no elevated contents of 1-butanol in German grape brandies could be determined.

Among the *alcohols* arising from the grape aroma, linalool, nerolidol, 4-terpinenol, and α-terpineol were detected. Concerning the amounts of the last mentioned compound, differences between the various grape brandy groups could be found.

Among the *carbonyls* the relative content of furfural shows a maximum in cognacs and a minimum in French grape brandies which corresponds to the derived expectations from the distillation methods (Hartmann, 1955) and the aging conditions (Wüstenfeld and Haeseler, 1964; Guymon and Crowell, 1963). The concentrations of this compound indicate that French grape brandies are produced continuously in column apparatus and are aged only for a short time. The high amounts of 2-pentanone, 2-heptanone, and 2-nonanone in German grape brandies are

partly related to the fact that these products acquire an intermediate position as far as the duration of aging process is concerned, during which the mentioned aroma substances show maximum values (Wüstenfeld and Haeseler, 1964). In the group of carbonyls, damascenone was detected and determined. Damascenone is a carotenoid degradation product already identified in wines (Schreier and Drawert, 1974) and rum (Smedt and Little, 1975) and is also formed during batch distillation involving pot stills (Schreier et al., 1979). This is also indicated by the amounts which are five–ten times higher in cognacs than in the other investigated groups of grape brandies. It is remarkable that during our investigations by mass spectrometry neither α - nor β -ionone were identified, aroma substances which were recently described in grape brandies by Litschew (1976).

As can be seen from Table II, in general cognacs do not contain higher concentrations of *acetals*. Some components of this chemical class, investigated especially in whiskey (Williams and Tucknott, 1972; Kahn et al., 1969) and rum (Liebich et al., 1970), exhibit maximal values in French grape brandies. The causes of these differences are not known.

Among the *lactones*, *cis*- and *trans*- β -methyl- γ -octalactone, aroma substances arising from oak wood during aging (Masuda and Nishimura, 1971), show maximal values in cognacs because of the long storage of these grape brandies. Otsuka and Zenibayashi (1974) investigated the sensory thresholds and the flavor characteristics of these substances and found a lower threshold value for the *trans* isomer (0.067 ppm) than for the *cis* isomer (0.79 ppm) which exhibits the more pleasant flavor. The usually determined higher amounts of *trans* isomer in distilled spirits (Otsuka et al., 1974; Litschew, 1976; Pisarnitzkij et al., 1976) are confirmed in this work. In a review article about lactones in fermented beverages, the occurrence and the biochemical pathways of these components are discussed in detail (Muller et al., 1973).

The so far determined amounts of neutral volatile aroma substances lead to the conclusion that quantitative differences between the individual groups of grape brandies occur especially among the components present in relatively low concentrations, a fact which can probably influence the final quality of the products.

The results of analytical separation and differentiation of the different groups of grape brandies by means of multiple discriminant analysis have been published elsewhere (Schreier and Reiner, 1979).

ACKNOWLEDGMENT

We are very grateful to Ing. (grad.) A. Junker for excellent technical assistance.

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Received for review September 6, 1978. Accepted November 13, 1978.