Odor Properties of 1-(p-Alkyl)Phenylethanols and Their Esters

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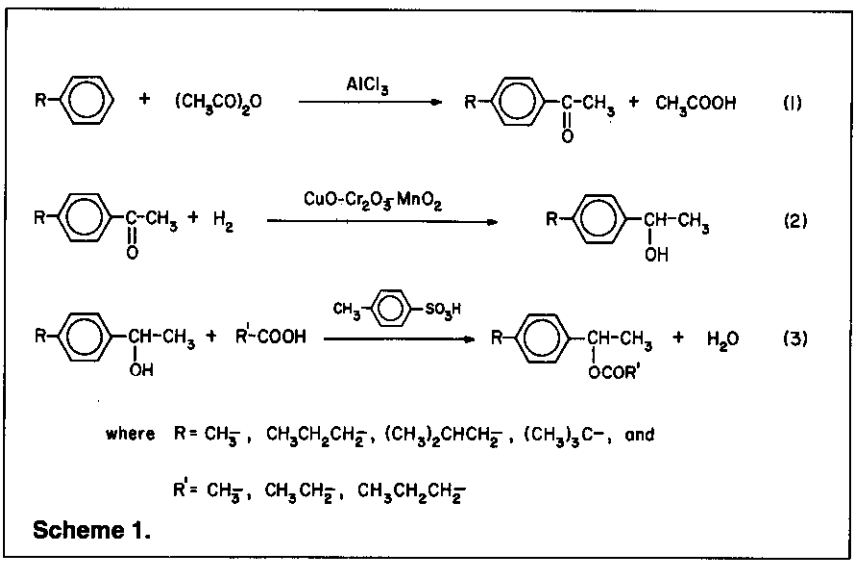
1-(p-Alkyl)phenylethanols were prepared by two-step synthesis: acylation of alkylbenzenes (alkyl = methyl, propyl, isobutyl, tert-butyl) and subsequent hydrogenation of the resulting p-alkylacetophenones. The resulting 1-(p-alkyl) phenylethanols as well as their esters have peculiar flavoring properties that suggest their use as fragrances.

Among the substances mentioned above, only p-methylacetophenone, p-isobutylacetophenone, p-tert-butylacetophenone and 1-(p-methyl)phenylethanol were considered as fragrances by Arctander.[1]

Special attention was paid to p-acetophenone derivatives, which can enrich the family of currently known flavors. Their preparation generally follows the reactions shown in Scheme 1.



Scheme 1.

Friedel-Crafts acylation of alkylbenzenes is usually carried with either chlorides or anhydrides of carboxylic acid using various acid catalysts.[2-8] In the present study we chose to use the method described in a patent whose authors claimed the method produced the highest yields.[7] The first reaction was followed by second and third steps performed in accordance with fundamental principles of hydrogenation and esterification reactions.[9,10]

Experimental Procedures

Table I lists the materials (and sources) used in this experiment.

Alkylbenzene acetylation to p-alkylacetophenones: 300 ml of dichloromethane were placed into a 1-liter distillation flask equipped with thermometer, stirrer, separating funnel and chlorcalcium glass closure. 100 g (0.825 mol) of $AlCl_3$ were added into the apparatus with intensive stirring. The reaction mixture was cooled down using an ice-salt coolant and the temperature was kept at –5° to 0°C. A reaction mixture of 36.3 ml of acetic anhydride (0.373 mol) and 58.6 ml of isobutylbenzene (0.375 mol) was added dropwise into the reaction vessel with intensive stirring and simultaneous cooling (–5° to 0°C, for 4 hrs.). Then the mixture was stirred for an hour at 0°C and for another hour at ambient temperature.

A 3-liter glass beaker filled with 500 g of ice in cold 35% HCl was employed for the decomposition step. The reaction mixture was poured onto crushed ice and allowed to stand overnight. The organic layer was washed with water to neutral reaction and separated, and a solvent was removed from the product. The crude product was purified by vacuum distillation. Other p-alkylacetophenones were prepared in a similar way.

Hydrogenation of p-alkylacetophenones to 1-(p-alkyl)phenylethanols: A 400 ml stainless autoclave equipped with manometer (0-24.5 MPa), magnetic two-

 0272-2666/93/0006-0041$04.00/0

Table I. Materials and suppliers for experimental procedures

Material	Supplier
propylbenzene	Aroma Zidovice
isobutylbenzene	Spolana Neratovice
tert-butylbenzene	Dept. of Organic Technology
p-methylacetophenone	Aroma Prague
acetic anhydride	Lachema Brno
acetic acid 99%	Lachema Brno
propionic acid	VEB Laborchemie Apolda, Germany
butyric acid	Astrid Prague
p-toluenesulfonic acid	Reachim, Russia
aluminum chloride	CHZ Litvinov
dichloromethane	CHEMA Prague
benzene	Lachema Brno
pentamethylenedithiocarbamate Cu^{2+} (polymerization inhibitor)	CHZ Litvinov
hydrogenation $CuO\text{-}Cr_2O_3\text{-}MnO_2$ catalyst (NIKKI N-203)	NIKKI Chem Co, Japan
hydrogen	Linde-Technoplyn Kyje

Table II. Physical properties of the prepared compounds

Code	Substance	b.p. °C/kPa	n^{20}_D
	p-Alkylacetophenones		
01	p-methylacetophenone	226/101.32	1.5335
02	p-propylacetophenone	94/0.3225	1.5240
03	p-isobutylacetophenone	97/0.3225	1.5186
04	p-tert-butylacetophenone	99/0.3225	1.5215
	1-(p-Alkyl)phenylethanols		
05	1-(p-methyl)phenylethanol	89/0.645	1.5222
06	1-(p-propyl)phenylethanol	108/0.7095	1.5135
07	1-(p-isobutyl)phenylethanol	112/0.645	1.5080
08	1-(p-tert-butyl)phenylethanol	111/0.774	1.4926^{70}
	Esters of 1-(p-Alkyl)phenylethanols		
09	1-(p-methyl)phenylethyl acetate	121/1.935	1.4955
10	1-(p-methyl)phenylethyl propionate	104/1.290	1.4930
11	1-(p-methyl)phenylethyl butyrate	110/1.161	1.4922
12	1-(p-propyl)phenylethyl acetate	114/1.161	1.4930
13	1-(p-propyl)phenylethyl propionate	121/1.419	1.4911
14	1-(p-propyl)phenylethyl butyrate	126/0.903	1.4901
15	1-(p-isobutyl)phenylethyl acetate	119/1.419	1.4902
16	1-(p-isobutyl)phenylethyl propionate	125/1.290	1.4891
17	1-(p-tert-butyl)phenylethyl acetate	121/1.290	1.4940

propeller stirrer, thermocouple probe and heating jacket was employed for hydrogenation reactions.

Typically 150 g of substrate (p-alkylacetophenone) and 3 g of NIKKI N-203 catalyst ($CuO\text{-}Cr_2O_3\text{-}MnO_2$) were introduced into the reactor. The vessel was closed tightly and flushed three times with hydrogen. Heating and stirring were started at a pressure of 980 kPa. At 140°C, the reactor was pressurized at 5.9 MPa and the reaction progress was followed by means of a pressure drop of hydrogen in the autoclave. When the pressure reached 4.9 MPa, the system was gradually pressurized to establish the initial value of 5.9 MPa. Absence of pressure drop indicated the reaction was over, after which mixing continued for half an hour. Then the reactor was cooled and opened, the catalyst was filtered and the product was purified by vacuum distillation.

Esterification of 1-(p-alkyl)phenylethanols: Acetates were synthesized in the third step by a reaction of acetanhydride with individual 1-(p-alkyl)phenylethanols. A three-neck glass flask (250 ml) equipped with reflux condenser, thermometer and sampling probe was used for the esterification reaction. A reaction mixture consisting of acetic anhydride (1.1 mol) and of 1-(p-alkyl)phenylethanol (1.1 mol) was placed into the reactor and the mixture was heated under reflux for two hours. After cooling, the mixture was vigorously shaken with water, then the organic phase was separated and purified by vacuum distillation.

For preparation of propionates and butyrates, a 250-ml

Table III. Odor character of the prepared compounds

Odor descriptor	Code:	Intensity (% of the scale) 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Odor acceptability[a]		50	44	54	55	46	59	47	54	48	54	58	53	52	57	57	48	54	64
Odor note intensity:[b]																			
Temperate zone fruits		23	35	42	9	18	9	27	14	25	33	38	-	-	-	13	25	28	14
Tropical fruits		38	43	53	29	28	22	52	26	38	35	45	42	51	40	37	39	36	22
Orange		22	30	22	11	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lemon, citrus fruits		19	31	20	20	17	7	30	18	22	25	20	-	-	-	-	-	-	-
Bananas		-	-	49	-	-	-	79	-	-	-	68	-	-	-	-	-	-	-
Pears, apples		-	-	67	-	-	-	-	-	28	32	30	-	-	49	28	21	30	18
Kiwi		-	-	-	57	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cantaloup		-	-	-	-	-	-	-	-	-	-	43	21	22	26	-	-	-	-
Cucumber		-	-	-	43	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Meadow flowers		14	22	17	14	16	8	24	14	15	24	20	22	24	24	24	21	22	13
Garden flowers		30	28	36	22	22	18	31	27	26	28	27	34	35	29	32	28	22	15
Room flowers		34	32	29	28	-	-	-	-	36	30	33	44	42	42	31	34	28	21
Aromatic		-	-	-	-	48	38	52	48	61	51	59	-	-	-	-	-	-	-
Woody		37	24	38	31	48	41	43	43	32	28	19	34	30	28	36	33	29	34
Moldy, decaying wood		-	-	-	55	-	-	-	-	-	-	-	-	-	-	15	17	8	-
Astringent, sawdust		-	-	-	-	40	30	34	41	-	-	-	-	-	-	-	-	-	-
Grassy, leaves		22	18	19	26	27	22	35	24	17	21	10	16	-	-	19	22	27	20
Decaying, moldy leaves		-	-	-	-	-	-	-	-	16	13	8	-	-	8	10	8	5	12
Honey-like		16	30	16	5	-	-	-	-	32	30	22	-	-	-	-	-	-	-
Sweet		40	-	43	-	-	-	53	-	44	41	43	-	-	-	-	-	-	-
Heavy		-	-	-	-	-	-	-	61	-	48	-	56	68	61	52	52	35	47
Warm		-	-	-	-	-	-	-	-	-	-	-	12	28	21	25	23	16	13
Hayish, straw-like		22	22	16	23	-	-	-	-	-	-	-	-	-	-	-	-	4	10
Ethereal		-	-	-	-	-	-	-	-	31	26	33	41	40	36	36	35	38	31
Spring-like		15	24	19	19	-	-	-	-	-	-	16	19	18	21	22	30	31	20
Fresh, green, minty, camphor		12	22	21	19	29	15	34	31	18	25	33	38	46	44	20	26	36	18
Rotten		7	3	17	17	15	25	12	7	2	3	19	11	7	21	7	3	7	18
Decaying, moldy hay		-	-	-	-	29	-	-	-	2	-	-	10	8	12	13	11	8	16
Moldy		-	-	73	-	28	22	-	-	5	5	11	9	3	15	5	4	6	16
Animal		-	-	55	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table III. Odor character of the prepared compounds

Odor descriptor	Code:	Intensity (% of the scale) 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Oily, rancid		9	6	15	14	-	26	10	75	10	13	-	-	-	-	-	-	-	-
Rancid		-	-	-	-	-	-	-	-	-	-	23	-	-	-	12	20	20	22
Soapy		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6	68	-
Dumpy		-	-	-	-	-	66	-	-	-	-	-	-	-	-	5	6	8	6
Wet paper, wet dog		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3	6	48
Buttery		5	9	11	6	7	6	13	7	4	7	13	-	-	40	5	-	-	-
Carob beans		7	11	25	8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Acetic, acidic		8	16	14	27	63	23	17	15	-	-	-	-	-	-	14	21	15	73
Metallic		8	7	11	6	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Penetrant, pungent		52	41	40	40	57	29	29	43	35	35	27	37	38	53	42	47	39	55
Sharp, biting		-	-	-	-	39	27	24	35	24	28	21	-	-	-	29	24	19	34
Staggering, dazing		-	-	-	-	-	-	-	-	50	42	53	54	63	63	46	53	38	35
Esteric		28	-	40	-	-	-	-	-	55	56	50	55	55	48	49	49	53	40
Liquorice		-	54	-	-	-	-	-	-	61	41	58	58	67	75	66	69	-	-
Melissa		-	68	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Anise		-	-	-	-	-	60	-	-	-	-	-	-	-	-	-	-	-	-
Onion		-	33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mushroom		-	-	-	-	-	-	-	-	-	54	-	-	-	-	-	-	-	-
Parsley root		-	-	-	-	-	-	-	-	21	19	8	-	-	-	-	-	-	-
Spicy		-	-	58	-	41	41	38	45	36	33	33	36	42	36	35	37	31	25
Painty		-	-	-	-	51	36	30	46	-	-	-	-	-	-	-	60	-	-
Terpenic		-	-	-	-	35	27	34	21	-	-	-	38	43	39	-	-	-	-
Plastics		-	-	-	-	-	36	-	-	-	-	-	-	-	-	-	-	-	-
Burnt rubber		-	-	-	-	-	56	-	-	-	-	-	-	-	-	-	-	-	4
Sweaty		-	-	-	-	-	53	-	-	-	-	-	-	-	55	-	-	-	-
Solvent-like		65	43	76	70	54	36	37	48	31	-	52	43	47	43	38	40	36	33
Furaldehyde		53	-	-	-	-	-	0	-	-	-	-	-	-	-	-	-	-	-

[a] On this scale, 0% = acceptable, 100% = unacceptable
[b] On this scale, 0% = imperceptible, 100% = very strong

Table IV. Odor perception thresholds in paraffin oil

Code	Perception threshold mg/kg	nmol/kg
01	1.99	14.8
02	151.5	933.9
03	39.9	226.4
04	224.0	1270.9
05	42.7	313.5
06	52.5	319.7
07	125.9	668.8
08	219.4	1230.8
09	125.7	705.3
10	513.0	2668.4
11	417.0	2021.6
12	165.8	803.8
13	282.2	1281.0
14	263.6	1124.9
15	75.9	344.5
16	316.3	1349.8
17	465.0	2110.8
18	955.0	4075.4

Table V. Volatilities of the substances tested immediately and hours after preparation

Code	Odor intensity (% of the scale)[a] immediate	after 1-2 hours	after 24-26 hours
01	91	58-75	2-24
02	73	77-81	4-31
03	54	59-64	0-13
04	40	44-48	0-16
05	46	61-75	4-18
06	49	63-77	34-45
07	42	38-40	20-22
08	40	51-62	0-14
09	56	47-52	0
10	26	51-75	0-9
11	29	56-83	0-27
12	41	43-45	16-33
13	37	42-46	0-3
14	49	45-47	6-25
15	47	32-40	0-12
16	56	25-41	15-20
17	51	59-67	6-22
18	37	50-63	17-20

[a] On this scale, 0% = imperceptible, 100% = very strong

glass flask supplemented with thermometer, sampling probe and azeotropic extension with reflux condenser was used. The carboxylic acid (1.2 mol), 1-(p-alkyl)phenylethanol (1 mol), benzene (50 ml), a few crystals of p-toluenesulfonic acid, and a small amount of polymerization inhibitor were heated under reflux until no further water was collected. The reaction mixture was thoroughly washed with water and $NaHCO_3$ solution, the solvent was removed by distillation, and the product was purified by vacuum distillation.

Analytical Methods

A gas chromatograph CHROM-5 with FID detector was employed to analyze the reaction mixtures and to follow the degree of conversion in the reaction. A glass column (2.5 m x 3 mm) packed with 15% Carbowax on Chromaton NAW-DMCS (0.16-0.20 mm) was used. Analyses were usually taken at 150°C.

The sensory analysis was carried out according to international standards[11] in a room equipped according to the standard requirements.[12] The group of 18 assessors was trained in agreement with the standard,[13] and the assessors had practical experience for at least six months, with particular emphasis on sensory profiling and rating with use of graphic scales. Immediately before each session, their performance was retested, and they were instructed both orally and in writing about the test procedure.

Odor character: The odor character was determined with the use of sensory profiling[14] by means of unstructured graphical scales[15] represented by straight lines 100 mm long, oriented by verbal description on the two ends (0% = imperceptible, 100% = very strong). The list of 20-30 odor descriptors was prepared by free choice description. The intensities were calculated as mean values of 18 responses. Standard deviations of the mean value varied between 2% and 5%. The odor acceptability was determined with use of a hedonic unstructured graphical scale (0% = acceptable, 100% = unacceptable). A sample was dissolved in paraffin oil (1.0% or 0.1% concentration) and the assessors evaluated it by sniffing from a 250-ml ground glass wide-neck bottle.

Odor perception thresholds: A set of solutions in paraffin oil was prepared, and the assessors sampled them in random order, with the exception of the strongest concentration which was presented as the first sample. Each sample was presented in a 250-ml ground wide-neck (35 mm) bottle. The assessors had to test the sample by sniffing, and to evaluate the odor perceived by using unstructured graphical scales (0% = imperceptible, 100% = very strong). The odor thresholds were calculated from the semi-logarithmic intensity-concentration plots. The results are means of 18 determinations.

Volatility of compounds: The samples (10%) were dissolved in ethanol, and smelling strips (150 mm x 5 mm) were impregnated with the solution. The strips were left free at room temperature of 22-23°C, and at the air humidity of 30-45%, protected from air currents, and the odor intensity was determined with use of unstructured graphi-

Table VI. Changes of the odor character of p-methylacetophenone (Code 01) during storage of the substance and of its ethanolic solution

Odor descriptor	Odor intensity (%) after days (d) of storage					
	8 d	17 d	27 d	8 d	17 d	27 d
	undiluted			20% ethanolic solution		
Odor acceptability[a]	39	43	42	35	39	38
Odor note intensity:[b]						
Temperate zone fruits	5	7	9	43	29	23
Tropical fruits	5	14	65	33	37	40
Oranges	7	5	33	21	25	26
Lemon	0	3	5	9	10	20
Meadow flowers	3	9	7	3	3	18
Garden flowers	2	15	35	52	47	55
Room flowers	21	24	85	48	55	48
Woody	83	77	67	14	30	30
Grassy, leaves	4	5	14	24	26	22
Honey-like	2	5	8	29	32	25
Hayish, straw-like	3	6	4	14	20	15
Spring reminding	3	1	4	6	10	10
Fresh, green	4	2	3	3	8	10
Rotten	14	13	32	6	2	16
Rancid	10	5	4	11	4	7
Buttery	2	2	7	8	5	8
Carob beans	8	10	10	10	7	8
Acetic, acidic	6	2	3	6	5	8
Metallic	17	17	3	3	3	1
Sharp, penetrant	42	60	55	67	59	49

[a] On this scale, 0% = acceptable, 100% = unacceptable
[b] On this scale, 0% = imperceptible, 100% = very strong

Table VII. Changes of the odor character of 1-(p-isobutyl)phenylethanol (Code 07) during storage of the substance and of its ethanolic solution

Odor descriptor	Odor intensity (%) after days (d) of storage					
	8 d	23 d	34 d	8 d	23 d	34 d
	undiluted			20% ethanolic solution		
Odor acceptability[a]	60	59	53	43	53	57
Odor note intensity:[b]						
Spicy	10	16	18	23	40	51
Woody	6	5	13	21	33	45
Astringent, sawdust	22	15	12	17	28	36
Meadow flowers	35	30	11	11	19	26
Garden flowers	38	52	42	49	54	58
Grassy, leaves	32	28	13	19	24	22
Temperate zone fruit	13	9	10	10	12	13
Tropical fruits	55	63	61	44	50	58
Aromatic	42	45	58	47	50	55
Lemon	10	10	12	15	10	13
Fresh, minty, camphor	7	6	7	16	23	24
Acid	6	10	13	10	19	22
Sharp, hot	8	5	10	21	34	40
Pungent	28	24	26	31	40	51
Rancid	41	33	27	33	31	30
Buttery	23	21	21	21	20	14
Rotten	41	48	41	22	17	20
Solvent-like, organic	27	24	27	30	23	26
Painty	13	14	17	12	16	21
Terpenic	25	25	29	29	29	34

[a] On this scale, 0% = acceptable, 100% = unacceptable
[b] On this scale, 0% = imperceptible, 100% = very strong

cal scales (0% = imperceptible, 100% = very strong) in the interval of 0-26 hours.

Odor stability: Samples and their 20% ethanolic solutions were stored at 60°C in 30-ml ground bottles. At defined time intervals, smelling strips (150 mm x 5 mm) were impregnated with the sample, and the odor character was determined 15 minutes after the impregnation.

Results and Discussion

p-Alkylacetophenones synthesis: Three p-alkylacetophenones (alkyl = propyl, isobutyl, tert-butyl) were prepared according to Friedel-Crafts synthesis. Their basic physical properties are given in Table II. p-Methylacetophenone was of commercial origin.

1-(p-Alkyl)Phenylethanol synthesis: There are different products of p-alkylacetophenone hydrogenation varying with diverse reaction conditions.[16-23] We focused our attention on preparation of 1-(p-alkyl)phenylethanols with the purpose of their subsequent use in esters synthesis.

Hydrogenation reactions were performed under conditions described by Cerveny et al.[23] Reactions proceeded selectively with high conversions (98%). We compared reaction rates of individual p-alkylacetophenones and concluded the rate decreased in the following sequence: p-methylacetophenone, p-propylacetophenone, p-isobutylacetophenone and p-tert-butylacetophenone. The reactions usually took 30-90 minutes. Yields of 1-(p-alkyl) phenylethanols were about 88-95% with 98.9-99.5% purity of products. Their physical properties are given in Table II.

1-(p-Alkyl)Phenylethanol esters synthesis: Table II summarizes physical properties of esters obtained from the experimental procedures described above. Low synthesized quantities caused considerable loss of esters, so we did not summarize their preparative yields. Their purity was 98-99%.

Odor characters: Odor characters of the prepared compounds are given in Table III. All the odors have complicated characters possessing fruity, floral, woody, grassy odor notes with small intensities of rotten, moldy notes. Some of them have characteristic odor notes, resembling cantaloup, bananas, soap, wet paper and similar off-odors. These minor odor notes could contribute to the fullness of

Table VIII. Changes of the odor character of 1-(p-methyl)phenylethyl acetate (Code 09) during storage of the substance and of its ethanolic solution

Odor descriptor	Odor intensity (%) after days (d) of storage					
	8 d	17 d	27 d	8 d	17 d	23 d
	undiluted			20% ethanolic solution		
Odor acceptability[a]	21	23	28	24	28	28
Odor note intensity:[b]						
Sweet	21	22	24	28	24	20
Honey-like	26	24	30	32	28	26
Apples, pears	33	36	40	30	33	33
Citrus fruits	15	25	35	25	23	20
Tropical fruits	19	21	28	32	28	25
Meadow flowers	39	45	42	36	42	45
Garden flowers	36	40	48	33	40	46
Room flowers	47	37	36	45	32	28
Aromatic	56	43	42	50	47	41
Esteric	38	39	40	35	40	52
Ethereal	33	31	31	30	33	44
Light, fresh	19	30	37	25	30	41
Grassy, leaves	28	30	34	30	32	44
Decaying leaves	3	4	3	5	3	1
Woody	3	4	8	4	4	3
Spicy	21	11	2	25	19	13
Parsley root	15	3	0	14	10	3
Buttery	3	4	3	5	2	1
Rancid	5	4	4	5	3	2
Rotten	2	2	3	3	1	1
Moldy	0	3	3	2	2	2
Sharp, hot	62	43	28	54	50	41
Irritant, pungent	47	41	22	44	41	28

[a] On this scale, 0% = acceptable, 100% = unacceptable
[b] On this scale, 0% = imperceptible, 100% = very strong

Table IX. Changes of the odor character of 1-(p-propyl)phenylethyl acetate (Code 12) during storage of the substance and of its ethanolic solution

Odor descriptor	Odor intensity (%) after days (d) of storage					
	8 d	23 d	34 d	8 d	23 d	29 d
	undiluted			20% ethanolic solution		
Odor acceptability[a]	58	44	42	53	35	31
Odor note intensity:[b]						
Light, fresh	15	27	34	26	53	66
Esteric	41	38	26	28	34	40
Ethereal	22	46	56	25	56	69
Terpenic	30	39	40	26	33	36
Spring-reminding, grassy	26	46	58	30	63	69
Meadow flowers	33	53	60	35	64	66
Garden flowers	43	39	18	22	30	32
Room flowers	40	23	7	29	4	3
Tropical fruits	24	20	7	18	4	3
Cantaloup	20	23	17	14	17	26
Heavy	35	23	14	29	17	23
Warm	19	18	18	15	7	8
Penetrant	42	39	42	37	44	32
Dazing, stupefying	45	36	20	34	19	21
Spicy	13	10	10	18	16	17
Woody	21	12	8	16	11	12
Organic, solvents	29	22	26	31	25	24
Rotten	17	19	10	14	3	5
Moldy	10	12	7	3	3	4
Decaying hay	30	17	12	17	14	20

[a] On this scale, 0% = acceptable, 100% = unacceptable
[b] On this scale, 0% = imperceptible, 100% = very strong

a composition, making it richer and more interesting, when they are added in small amounts.

Odor perception thresholds: Odor perception thresholds of the substances in paraffin oil are summarized in Table IV. The perception thresholds are medium in most substances, with the exception of the lowest MW ketone. Among the ketones, the isobutyl homologue has a particularly low threshold. The corresponding alcohols have low perception thresholds, especially the methyl homologue, but on the contrary, the isobutyl homologue has a higher threshold than the corresponding ketone. Esters prepared from the methyl derivative have higher thresholds than the corresponding alcohols (even when expressed on an equimolar basis).

Volatilities: Volatilities of the substances are given in Table V. The volatility of some substances is very low. Usually, some time is necessary to develop the maximum odor intensity on the smelling strip. In case of alcoholic derivatives and esters containing larger alkyl substituents, the volatility was very low, and the odor was perceptible after more than 24 hours. Esters of methyl homologues were more volatile. The volatility of the ester derivatives cannot, however, be explained on the basis of molecular mass and polarity only.

Odor stabilities: Stabilities of several of the substances tested under conditions of accelerated storage with access to air are given in Tables VI through X. As is evident from these tables, the odor character is not much changed by storage under accelerating conditions (1 day at 60°C corresponds to about 1 month at room temperature). Changes within about six months storage are negligible, and only after rather long storage time would the character change moderately. Changes in the ethanolic solutions are slightly more rapid, but even in ethanol, the odor character does not change appreciably. It should be noted that substances discussed in this paper would be only minor components in the fragrance composition. Changes due to transesterification in ethanol should be considered in cosmetic products pos-

Table X. Changes of the odor character of 1-(p-isobutyl)phenylethyl acetate (Code 15) during storage of the substance and of its ethanolic solution

Odor descriptor	Odor intensity (%) after days (d) of storage					
	8 d	17 d	27 d	8 d	17 d	27 d
	undiluted			20% ethanolic solution		
Odor acceptability[a]	43	49	44	36	45	51
Odor note intensity:[b]						
Esteric	45	52	65	50	53	46
Ethereal	24	39	41	41	33	22
Meadow flowers	5	15	26	22	16	4
Garden flowers	12	33	68	48	37	27
Room flowers	78	78	78	58	57	61
Apples, green	9	6	8	14	12	16
Tropical fruits	69	68	68	70	68	68
Heavy	68	71	73	48	66	84
Warm	51	54	60	36	43	57
Woody	10	9	8	18	24	21
Spicy	18	29	27	36	42	43
Acidic, acetic	4	3	4	8	6	8
Fresh, light	2	2	2	6	5	5
Mown grass	2	3	4	4	3	4
Sharp, penetrant	4	16	22	21	29	31
Stupefying, dazing	61	66	70	44	55	87
Rancid	24	23	13	34	24	21
Decaying hay	37	29	26	40	35	20
Rotten	26	18	15	24	20	18
Moldy	36	30	26	39	33	32
Organic, solvents	12	14	20	22	24	29

[a] On this scale, 0% = acceptable, 100% = unacceptable
[b] On this scale, 0% = imperceptible, 100% = very strong

sessing lower pH values. All the substances should thus be considered as relatively stable.

Conclusions

All the substances have, principally, similar odor characters, possessing fruity, flowery, woody, penetrant odor notes with minor rotten, moldy notes. Other characteristic notes were observed in some compounds.

Odor thresholds show mostly medium values, suitable for application in perfumery products.

The volatility is rather low so that the substances are suitable as the non-volatile basis for perfumes.

All substances were found to be rather stable both on storage in pure state or in ethanolic solutions. Changes in the odor character are moderate and slow (taking place after ten days on average at 60°C).

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