

Demonstrating perfume fixation

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Techniques for the quantitative proof of perfume fixation do not exist in the literature, partly because perfumery is considered more art than science and is rarely discussed in quantitative terms and partly because such a technique would likely be quite difficult and tedious. We undertook the challenge of developing a meaningful, reproducible procedure capable of quantifying fragrance fixation in order to demonstrate this characteristic in a 20 mole propoxylate of methyl glucoside^a (fig. A), which had previously demonstrated a strong fixative character in consumer panel testing.¹

It is fair to say that the usual toilet water or toiletry fragrance contains more than one hundred separate chemical entities. In order to evaluate a fixative effect on a heterogeneous mixture such as the typical fragrance composition, it was decided to select several individual fragrance chemicals derived via synthesis or isolation from natural products, covering a broad range of chemical structures and boiling points.

EXPERIMENTAL PROCEDURE

Evaporation Procedure

Perfume blotters are spotted with 1 mg of an aroma compound with and without 1 mg of the fixative.^a The methanolic solution of the aroma compound, with and without the fixative is applied to the top of these perfume blotters by means of a 10 μ l syringe or micropipettor. These blotters are then placed in a "fish tank" where

they are allowed to evaporate at ambient room temperature, pressure and humidity, for periods of 1 hr, 3 hrs, 6 hrs and 24 hrs. At the end of each specified time period, the top portion of each blotter is cut off and placed into a suitable vial or flask containing methanol. The aroma compound is extracted from the blotter with methanol. The resulting solution is then appropriately analyzed by GLC or UV.

GLC Procedure

Each perfume blotter strip is extracted with 1.00 ml of methanol containing 1 mg of an "internal standard" for more reliable quantitation. The amount of aroma compound in each blotter solution is determined by comparing the GLC response ratio of aroma compound/internal standard in the blotter solution to a standard solution deliberately prepared to have a similar response ratio. A number (2 to 4) of GLC injections of each blotter and standard solution are made and the results are averaged.

UV Procedure

Each perfume blotter strip is extracted with from 2 to 100 ml of methanol, depending upon the UV absorption of each individual aroma compound. The amount of aroma compound in each blotter solution is determined by comparing the UV absorbance of each blotter solution to a standard solution. The amount of aroma compound in each solution is proportional to the absorbance of each solution.

Zero-Time Determinations—GLC Procedure

Ideally, the "zero time" perfume blotters should be spotted under exactly the same conditions as the other blotters have been spotted, then extracted with methanol before any of the aroma compound can evaporate. If a perfume blotter is spotted in the open, even if it is immediately immersed in methanol, some aroma compound will be lost. This was shown in an

^aGlucam P-20, a registered trade name of Amerchol Corporation.

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Demonstrating perfume fixation

experiment with eugenol, a moderately volatile compound. Thus, the aroma compound had to be spotted and then extracted with methanol in a closed system.

A perfume blotter strip was attached to the under side of a split plug septum by means of a very small straight pin. 1.00 ml of methanol containing 1 mg of an internal standard was added to a vial, which was then covered with the septum containing the blotter strip and sealed closed. The perfume blotter strip was then spotted with the aroma compound by injecting through the septum cap with a 10 μ l syringe, then extracting with the methanol solution and analyzing.

Zero-Time Determinations—UV Procedure

As with the GLC procedure, a split plug septum was used, which could be washed free of methanol-soluble UV absorbers. The UV procedure was similar to the GLC procedure except that from 2 to 100 ml of methanol, depending upon the UV absorption of each individual aroma compound, was used in the extraction without an internal standard.

A total of forty-nine individual fragrance chemicals were subjected to the above procedures. (The list had been slightly larger but some of the materials proved to be too unpleasant to work with when volatilized in the confines of the laboratory.) The boiling points of the materials ranged from 142°C to over 350°C. Basic hydrocarbon roots included aliphatic, aromatic, terpenoid, bicyclic, and heterocyclic. Basic functional groups included esters, aldehydes, acetals, alcohols, olefins, ketones, ethers, phenols, lactones, and glycidates. The identities were sufficiently diverse so that if a pattern emerged with the forty-nine materials tested, there was good reason to assume that it could be applied across the broad spectrum of the hundreds of fragrance chemicals used in perfumery. In a

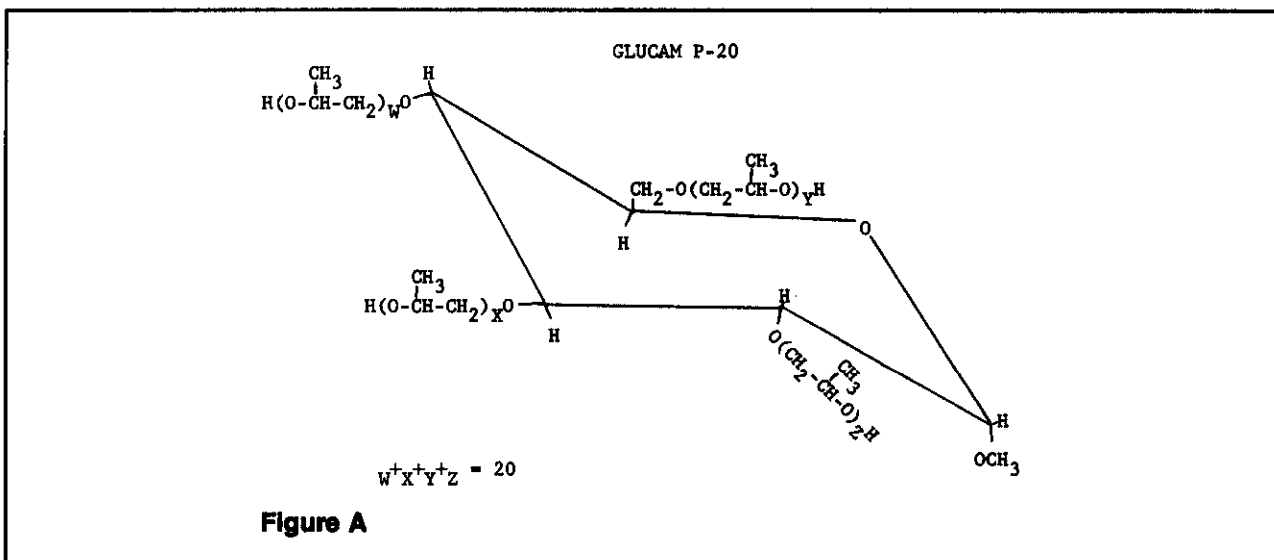
number of cases, the test was run several times to check reliability and also to test various conditions. These techniques were tested a number of times and as skill was acquired, reproducible results within plus or minus 10% were achieved.

It was learned, for instance, that variations in temperature, pressure, and humidity could have an effect on the absolute reading of the unevaporated material remaining on the blotters. However, it was interesting to note that while the absolute numbers differed, the numerical relationships of the unevaporated material retained within the evaporation periods from one to twenty-four hours remained constant. Therefore, it was decided not to complicate the procedure further by requiring specially controlled evaporation chambers, but rather to record the environmental conditions during the test and investigate results that appeared to be anomalous. Experience with dozens of runs indicated that the procedure was meaningful and reproducible without the need for special chambers and conditions, which would have slowed an already tedious procedure considerably.

Results

Table I is a complete tabulation of the experimental results. The aromatic chemicals in this table are listed in ascending order of boiling point. While not all the boiling points are exact, for the purposes of this study they serve as very useful guides. Where the symbol "+" or "-" is used, it implies that no boiling point was found in the literature, and that the approximate boiling point listed positions it properly in the table. In actual practice the great majority of the materials listed are distilled at reduced pressures since they tend to decompose at their boiling points.

After the boiling point column, there are four double columns under the overall heading of "Percentage Unevaporated." Each double column is headed by a time in hours, specifically



Demonstrating perfume fixation

Table I

	Boiling Point °C @ 760mm	Percent Unevaporated							
		1 hour		3 hours		6 hours		24 hours	
		T	U	T	U	T	U	T	U
Isoamyl Acetate	142	1	1	-	-	-	-	-	-
n-Propyl Acetal	143	4	5	-	-	-	-	-	-
Alpha Pinene	156	16	12	8	6	-	-	-	-
Benzaldehyde	180	20	23	20	22	18	20	15	15
Linalool	199	29	6	4	5	3	3	3	3
Acetophenone	202	8	6	< 1	< 1	-	-	-	-
Citronellal	206	40	17	9	9	7	10	5	6
n-Decyl Aldehyde	208	40	19	16	14	16	13	14	5
Allyl Caproate	± 210	3	5	3	5	-	-	-	-
Benzyl Acetate	215	46	11	2	-	-	-	-	-
Menthol	216	45	25	16	10	4	5	2	3
Alpha Terpineol	217	58	38	19	11	5	8	-	-
Phenylethyl Alcohol	219	82	79	57	51	31	26	2	2
Linalyl Acetate	220	43	8	1	1	1	1	1	1
Methyl Salicylate	221	18	19	9	10	9	11	8	9
Isobornyl Acetate	225	40	17	2	2	< 1	< 1	-	-
Menthanyl Acetate	227	32	12	1	1	-	-	-	-
Citral	229	63	41	27	23	7	8	5	7
Geraniol	229	94	56	62	44	52	36	-	-
n-Decanol	231	55	67	38	37	40	23	3	5
Trans Anethole	233	50	25	10	8	7	10	6	8
Linalyl Butyrate	235	74	65	32	8	6	1	-	-
Safrole	236	64	36	16	< 1	-	-	-	-
Caryophyllene	240	68	56	24	1	-	-	-	-
Geranyl Acetate	242	82	74	55	32	44	20	25	26
Hydroxycitronellal	250	72	57	53	36	33	9	6	2
Indole	252	75	51	55	36	45	20	19	3
Methyl Nonyl Acetaldehyde (Aldehyde C-12M)	252	54	3	4	1	-	-	-	-
Cinnamic Aldehyde	253	77	68	47	28	27	20	16	18
Eugenol	253	91	65	76	33	58	21	21	16
Diphenyl Oxide	255	68	61	38	10	13	3	1	1
Methyl Anthranilate	255	94	95	71	35	52	28	20	21
Cinnamic Alcohol	258	89	85	82	67	74	54	37	27
Beta Ionone	± 260	98	95	79	69	55	35	4	1
Heliotropine	263	87	88	72	73	51	47	28	32
Aldehyde C-18 (Gamma nonalactone)	263	88	87	67	62	47	32	9	10
Aldehyde C-16 (Ethyl Methyl Phenylglycidate)	271	97	95	94	88	94	65	51	29
Yara Yara (Beta Naphthyl Methyl Ether)	274	89	82	50	48	47	24	4	5
Amyl Salicylate	280	95	86	85	73	67	44	10	1
Vanillin	285	85	89	62	56	60	42	60	46
Vetiverol	± 285	84	82	76	69	71	67	69	66
Amyl Cinnamic Aldehyde	290	102	98	93	90	89	80	54	32
Ethyl Vanillin	± 295	101	100	98	102	94	100	97	93
Aldehyde C-14 (Gamma Undecalactone)	297	100	100	98	97	87	91	74	66
Santalol	301	109	110	108	110	110	106	101	86
Coumarin	302	107	104	95	85	89	90	64	55
Benzyl Benzoate	323	95	94	93	91	93	91	84	76
Aurantol	> 325	95	100	86	92	75	70	42	38
Benzyl Cinnamate	350	101	99	101	102	100	98	102	99

Demonstrating perfume fixation

1,3,6 and 24. Within each time column there are two columns, one labeled "T," meaning that it has been treated with the fixative, and one labeled "U," meaning that nothing has been added to the fragrance materials. The numbers in each column represent the percentage of material remaining on the blotter, subsequently extracted and measured for each fragrance chemical in each time area. Wherever there is a dash, it means that no detectable amount of the material could be extracted and that it effectively is a zero.

The first entry in the table is Isoamyl acetate with a boiling point of 142°C. After one hour with both the treated and untreated materials only 1% remained on the blotter. Beyond that, no material was detected. This material is so fleeting that nothing can serve to fix it significantly.

The last entry in the table is benzyl cinnamate with a boiling point of 350°C. In this case all the readings, treated or untreated, one hour or twenty-four hours, are essentially 100%. This material is so nonvolatile that it does not require fixing. Just within these two extremes are a number of materials that tend to show relatively little effect by the fixative. There is, however, a larger number of materials that show varying and frequently dramatic effects.

Citronellal has a relatively low boiling point of 206°C. However, 40% of it is retained after one hour of evaporation when treated, while only 17% of the untreated material remains. This implies a very significant effect on the citronellal note, particularly in the early stages of its presence on the wearer's skin. After three, six, and twenty-four hours, both the treated and untreated show unevaporated residues of 10% or less, implying that most of the effect of the materials is gone after a couple of hours and fixation is no longer a question. But the effect in the first hour, which is the most significant period to the wearer, is dramatic.

Benzyl acetate is a common workhorse ingredient in many floral fragrances, with a boiling point of 215°C. After one hour, the treated material retains 46% of its strength while the untreated material drops to 11%. After three hours, the benzyl acetate is essentially gone, but here too, its effectiveness in that critical period is demonstrated. Linalyl acetate, another staple in many perfume compositions, retains 43% of the treated material after one hour while the untreated is down to 8%. It too is essentially gone after three hours. Similar results are noted for isobornyl acetate and menthanyl acetate. As the boiling points continue to climb, the basic pattern persists but changes in total duration of fragrance begin to show.

Citral shows greater than 60% retention when treated and about 40% when untreated. This is a significant differential and means that good retention is obtained in that early critical stage of

fragrance perception by the user. After three hours there is no longer the complete disappearance of the fragrance component seen in lower-boiling chemicals, and there is a leveling off in the difference between treated and untreated. By the time the six-hour level is reached, most of the material is gone.

For geranyl acetate the difference between the treated and untreated after one hour is 8% but after three hours the difference becomes more significant, 55% for the treated and 32% for the untreated. The same relationship continues at six hours, 44% compared to 20%, and then levels off without complete loss after twenty-four hours to approximately 25% for both treated and untreated.

Hydroxycitronellal boils at 250°C and shows a smooth, steady relationship between the treated and untreated: significant after one hour, more pronounced after three and six hours, and still showing after twenty-four hours.

Methyl nonyl acetaldehyde has a boiling point of 252°C but demonstrates a very dramatic difference in behavior compared to other materials boiling in the same general range. After one hour the treated material remains 54% unevaporated whereas the untreated material has lost all but 3%. After three hours the material is essentially gone. The result may appear to be anomalous, but it may also mean that there is more to the entire phenomenon than mere vapor pressure depression. While one could theorize all sorts of mechanisms, such as acetal formation or other types of bonding, suffice it to say that the empirical results show an unusual effect with this branched chain aliphatic aldehyde.

Eugenol and diphenyl oxide are in the same general boiling range as hydroxycitronellal and methyl nonyl acetaldehyde, but they tend to conform to the pattern shown by hydroxycitronellal. They very clearly demonstrate a quantitative fixative effect.

Yara yara has a boiling point of 274°C and shows a very low loss on evaporation after the first hour. There is a modest effect at one hour and no significant effect after three hours. A more meaningful effect is noted after six hours with almost complete loss after twenty-four hours. Vetiverol, with an approximate boiling point of 285°C, shows that the material requires no added fixation for high retention. After one hour, treated or untreated, approximately 80% remains. Even after twenty-four hours the figures are 69% for the treated and 66% for the untreated. This effect becomes more pronounced with aldehyde C-14, with the bulk of the material still there after twenty-four hours. Ethyl vanillin demonstrates very little volatility, with losses of only 3% to 7% after twenty-four hours. Returning to the table, materials such as the sesquiterpene alcohol, santalol, show essentially no evaporation losses in the twenty-four hour period.

Conclusions

Quantitative evidence of fragrance fixation by a 20 mole propoxylate of methyl glucoside^b was obtained by subjecting a representative series of pure aroma chemicals to accurately measured evaporation and retention studies over time segments of 1,3,6 and 24 hours. The number and variety of aroma chemicals studied permits application of the results to most of the remaining aroma chemicals in the perfumer's repertory. Improved fixation is possible at very modest cost with this simple application technology. When used for this purpose, it will also provide significant added benefits:

Emollient and Humectant Properties

As do most polyols, this glucoside attracts moisture, but in addition, it serves as an emollient (skin softener, moisturizer). Thus, it may replace traditional humectants such as glycerine, propylene glycol, or sorbitol, and play a multiple role.

Sting Reduction

The addition of this glucoside to alcoholic or hydroalcoholic extracts (aftershave, cologne, bath splash) normally applied over large, sensitive skin areas significantly reduces the usual stinging sensation, and reduces the typical pungency of perfume grade alcohol. This is in addition to providing fragrance fixation, cost savings, humectancy, and emollience.

Ease of Incorporation

PPG-20 methyl glucose ether is readily soluble with simple stirring in alcohol and water in all proportions. It can be mixed with many perfume oils, except those rich in hydrocarbons. It is readily formulated into a wide variety of fragrances, cosmetics, toiletries and chemical specialty products.

Renewable Source

PPG-20 methyl glucose ether is derived from starch via glucose, a plentiful and renewable vegetable source.

Acknowledgement

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References

1. A. Seldner, Glucose Derivatives in Emollient Skin Care Formulations, *Cosm. Toil.*, **93** (3), 73 (March) 1978
2. A. Seldner, United States Patent 4,264,478, Polyol Fragrance Fixatives, issued April 28, 1981, assigned to Amerchol Corporation

^bGlucam P-20