hydrogenase converts part of the acetaldehyde into ethyl alcohol, but possibly its role may be indirect by maintaining the reduced diphosphopyridine nucleotide in an oxidized form, permitting further glycolysis.

References

(1) Arighi, A. L., Joslyn, M. A., and Marsh, G. L., *Ind. Eng. Chem.*, **28,** 595 (1936).
(2) Assoc. Offic. Agr. Chemists, Washington, D. C., "Methods of Analysis," 7th ed., 1950.
(3) Bailey, L. H., "Manual of Cultivated Plants," New York, Macmillan Co., 1949.
(4) Balls, A. K., and Hale, W. S., *J. Assoc. Offic. Agr. Chemists*, **15,** (3), 483 (1932).
(5) Barker, J., and ElSaifi, A. F., *Proc. Roy. Soc. (London)*, Ser. **B, 140,** 900 (1952).
(6) Berger, J., and Avery, G. S., *Science*, **98,** 454 (1943).
(7) Buck, P. A., M.S. thesis, University of California, 1948.
(8) David, J. J., Ph.D. thesis, University of California, 1949.
(9) Joslyn, M. A., *Advances in Enzymol.*, **9,** 631 (1949).
(10) Joslyn, M. A., *Food Inds.*, **18,** 1204 (1946).
(11) Joslyn, M. A., and David, J. J., *Quick Frozen Foods*, **15** (No. 4), 51 (1952).
(12) Lee, F. A., and Wagenknecht, A. C., *Food Research*, **16,** 239 (1951).
(13) Singer, T. P., and Pensky, J., *Biochem. et Biophys. Acta*, **9,** 316 (1952).

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VANILLA-LIKE SYNTHETICS

Solubility and Volatility of Propenyl Guaethol, Bourbonal, Vanillin, and Coumarin

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Flavor studies on the vanilla-like synthetics, propenyl guaethol, bourbonal, vanillin, and coumarin, required an extension of the literature information on their solubilities and volatilities. The solubility of propenyl guaethol, in per cent by weight at 24° C., was found to be 0.002 in water, 0.54 in 50% ethanol by weight, 16.7 in 100% ethanol, 0.11 in 50% propylene glycol by weight, and 4.00 in 100% propylene glycol. In water, the solubility of bourbonal in per cent by weight at 25° C. was found to be 0.35, of vanillin 1.24, of coumarin 0.222, and of propenyl guaethol 0.0022. The relative volatilities over the range 24° to 105° C. are, in increasing order, bourbonal, vanillin, propenyl guaethol, and coumarin. However, the differences are not considered significant for flavoring purposes. The data on solubility and volatility of the synthetic vanilla-type flavoring materials are useful in preparing solutions of these compounds for use as flavor concentrates and in estimating their probable loss through volatilization during cooking.

RECENT FLAVOR STUDIES (*1*) of the high-flavor-strength, vanilla-like synthetic, 5-propenyl guaethol, in comparison with bourbonal (ethylvanillin), vanillin, and coumarin, required knowledge of solubilities in water, ethanol, propylene glycol, and mixtures thereof for each of these compounds, and of their relative volatilities.

Nothing on volatility, and not enough on the desired solubilities, was found in the literature. Some information, mostly qualitative, on the solubility of vanillin and coumarin appeared in the usual handbooks. One trade bulletin (*4*) gave solubility tables for bourbonal, vanillin, and coumarin, while another (*5*) gave some solubility data for propenyl guaethol. Mange and Ehler (*3*) reported solubilities of vanillin in alcohol-water and glycerol-water solutions, describing in detail their methods of determination, and noting especially the danger of error due to supercooling.

A simplified adaptation of the methods of Mange and Ehler was used to obtain additional solubility data for immediate use. Comparative volatilities of the four compounds were simply determined at several temperatures. It is hoped that the methods and data here reported will prove useful, and especially that they will stimulate further work in this neglected field.

Samples and Solvents

All synthetic flavoring materials used were commercial samples as currently offered for use in foods.

Propenyl guaethol, 1-ethoxy-2-hydroxy-4-propenylbenzene or 5-propenyl guaethol, was purchased from Shulton, Inc., under the trade name Vanitrope.

Bourbonal, 3-ethoxy-4-hydroxybenzaldehyde, also known as ethylvanillin and as vanillal, was purchased from Monsanto Chemical Co. under the trade name Ethavan.

Vanillin, 3-methoxy-4-hydroxybenzaldehyde, was from Monsanto.

Coumarin, *o*-hydroxycinnamic acid lactone, was from Monsanto.

Distilled water and U.S.P. XIV grades of absolute alcohol and propylene glycol were used as solvents.

Experimental Methods

The method used for solubility determinations, adapted from the work of Mange and Ehler (*3*), requires only simple laboratory equipment, guards against supercooling errors, and appears to be convenient and efficient for general application.

Each solubility curve was first roughly determined by a few trials and then verified at a number of points by more accurate determination. As an illustration, the determination of the approximate solubility curve for propenyl guaethol in ethanol-water solutions at 24° C. is described.

To approximately 0.05 gram of propenyl guaethol, accurately weighed in a 2-ounce glass bottle with an aluminum foil–lined screw cap, was added slightly less than the required quantity of ethanol. After weighing, the solution was warmed with shaking until clear, then cooled to 24° C., resulting in crystal

Table I. Solubility of 5-Propenyl Guaethol in Water-Ethanol at 24° C.

Ethanol in Solvent		Density, G./Ml.		Propenyl Guaethol Solubility	
% by wt.	% by vol.[a]	Solvent[a]	Solution[b]	% by wt.	G./100 ml. solution[b]
0	0.00	0.99732	0.997	0.002	0.002
5	6.25	0.98839	0.988	0.005	0.005
10	12.40	0.98067	0.981	0.011	0.011
15	18.48	0.97373	0.974	0.023	0.022
20	24.49	0.96686	0.967	0.044	0.043
25	30.40	0.95952	0.960	0.077	0.074
30	36.20	0.95134	0.951	0.125	0.12
35	41.85	0.94221	0.942	0.19	0.18
40	47.35	0.93226	0.932	0.28	0.26
45	52.75	0.92166	0.922	0.38	0.35
50	57.90	0.91064	0.911	0.54	0.49
55	62.90	0.89933	0.901	0.82	0.74
60	67.70	0.88783	0.890	1.30	1.16
65	72.38	0.87614	0.880	2.04	1.80
70	76.94	0.86429	0.870	3.07	2.67
75	81.31	0.85224	0.861	4.40	3.79
80	85.49	0.83997	0.853	6.04	5.16
85	89.49	0.82741	0.846	8.0	6.77
90	93.27	0.81437	0.840	10.3	8.65
95	96.78	0.80063	0.835	13.1	10.9
100	100.00	0.78592	0.832	16.7	13.9

[a] From (2).
[b] Calculated.

formation. The additional solvent required was estimated, slightly less was added, and the solution was warmed to effect solution, then cooled to 24° C., resulting in the formation of fewer crystals. After a few such trials, a point was reached where no crystals were formed even upon seeding with the solute. The true solubility, therefore, lay within the narrow range between the values calculated before and after the last small increment of solvent.

Further points on the curve were obtained by adding more ethanol to the solution, weighing, adding enough distilled water to produce a slight permanent precipitate, weighing, and then adding barely enough alcohol to dissolve the precipitate. In this manner, enough tentative data were provided for the solubility curve down to 25% ethanol by weight. As the solubility of propenyl guaethol had now dropped to about 0.05% by weight, it was possible to draw a fairly accurate curve.

The tentative solubility curve was then checked and corrected at suitable points by the following procedure. For a given point, three bottles, each containing the calculated weight of solute for 50 grams of solution, were prepared. To one, the calculated quantity of solvent mixture was added; to the second, 2% more than the calculated quantity of solvent; and to the third, 2% less than the calculated quantity of solvent. Crystals usually formed in one or two of the solutions after warming, shaking, cooling to 24° C., and seeding, if necessary. In a few cases, crystals appeared in all or none, whereupon another solution was prepared with 2% more or less solvent, as indicated. An estimate of the remaining crystals permitted the calculation of the true point of the solubility curve to an accuracy of at least ±2%.

The solubility curve for propenyl guaethol in aqueous solutions of propylene glycol was similarly determined at 24° C. However, supercooling proved to be more troublesome in this case. All the work at 24° C. was performed in a conditioned room at 24° ± 1° C. The temperatures of the solutions were maintained at 24° ± 0.5° C.

The temperature-solubility curves were determined in much the same manner. The known amount of solute was dissolved in slightly less than the required amount of solvent for complete solution at 50° C. After warming to dissolve and then holding at 50° C. until the formation of crystals, the solution was cooled to 24° C., an estimated increment of solvent was added, and solution was effected by warming above 50° C. Again, if no crystals formed, the solution was seeded at 50° C. A point on the tentative solubility curve was thus fixed between the last concentration at which crystals formed and the slightly lower concentration at which no crystals formed on seeding.

Further points at lower temperatures, down to 6° C., were similarly established with the addition of more solvent. The tentative curve was drawn, and suitable points were checked and corrected in a manner similar to that described above for varying solvent composition.

A forced-draft electric oven was used for temperatures above 24° C., and an electric refrigerator for determinations at 6° C. The temperatures of the solutions were maintained to ±0.5° C. during each determination.

By this method, solubilities of propenyl guaethol, bourbonal, vanillin, and coumarin in water, and of propenyl guaethol in 50% propylene glycol by weight and in 33.35% ethanol by weight (40% by volume), were determined over the range 6° to 50° C.

In the present case, major interest in relative volatility of the flavoring compounds was in the range 50° to 100° C. As no data were found in the literature, some very limited experimental determinations were made. Prior to these,

Table II. Solubility of 5-Propenyl Guaethol in Water–Propylene Glycol at 24° C.

Propylene Glycol in Solvent, % by Wt.	Density of Solvent, G./Ml.	Propenyl Guaethol Solubility, % by Wt.
0	0.997	0.002
10	1.001	0.005
20	1.005	0.012
30	1.009	0.026
40	1 013	0.053
50	1.017	0.11
60	1.021	0.24
70	1.025	0.48
80	1.029	0.95
90	1.033	1.89
100	1.037	4.00

Table III. Solubility of 5-Propenyl Guaethol in Water, Aqueous Propylene Glycol, and Aqueous Ethanol, and of Bourbonal, Vanillin, and Coumarin in Water

Temp., °C.	Solubility, Per Cent by Weight					
	5-Propenyl guaethol in			Bourbonal in water	Vanillin in water	Coumarin in water
	Water	50% P.G.[a]	40% EtOH[b]			
0	0.0011	0.025	0.050	0.15	0.50	0.088
5	0.0012	0.035	0.065	0.17	0.60	0.106
10	0.0013	0.049	0.085	0.20	0.72	0.128
15	0.0015	0.068	0.110	0.24	0.86	0.154
20	0.0018	0.092	0.140	0.29	1.03	0.185
25	0.0022	0.121	0.175	0.35	1.24	0.222
30	0.0027	0.155	0.215	0.42	1.50	0.266
35	0.0034	0.195	0.260	0.50	1.82	0.319
40	0.0044	0.240	0.312	0.62	2.22	0.381
45	0.0059	0.290	0.374	0.78	2.70	0.453
50	0.0080	0.350	0.450	1.00	3.30	0.540

[a] Water–propylene glycol; 50% propylene glycol by weight.
[b] Water–ethanol; 40% ethanol by volume, 33.35% by weight.

Table IV. Melting Points and Relative Volatilities of 5-Propenyl Guaethol, Bourbonal, Vanillin, and Coumarin

	5-Propenyl Guaethol	Bourbonal	Vanillin	Coumarin
Melting point, °C.				
Closed capillary	85.5	78.0	82.0	68.0
Literature range	85–86	76.5 min.	81–82	67–70
Relative volatility, mg./sq. cm./hour				
24° C.[a]	0.0005	0.0003	0.0004	0.0016
50° C.	0.06	0.04	0.05	0.08
70° C.	0.18	0.10	0.12	0.21
90° C.	0.75	0.43	0.47	0.80
105° C.	1.80	1.03	1.14	1.90

[a] As determined in 55-mm. aluminum dishes; all other volatilities determined in 8-mm. glass petticups.

closed capillary melting points were run on the samples used.

Determinations of relative volatility above room temperature were actually run at 50°, 70°, 90°, and 105° C. in a forced-draft electric oven. Since this range extended well above the melting points of all of the compounds, duplicate samples of 0.1 to 0.2 gram of each compound were weighed into glass "petticups" (flat-bottomed glass cylinders, 8 mm. in inside diameter, 15 mm. high) and placed in an oven at 105° C. At intervals of 24 hours the petticups were removed, cooled, and weighed, until a substantially constant rate of loss had been established for each compound. The temperature was lowered to 90° C., and weighings were repeated at intervals of 1 to 2 days.

The temperature of the oven was then lowered to 70° C., at which temperature all the compounds except the coumarin were solid, and the procedure was repeated, with the period between weighings increased to 5 to 7 days. Then the temperature was lowered to 50° C., where all of the compounds were solid, and the procedure was repeated, with the period between weighings extended to 10 to 20 days.

Finally, as a check on relative volatility at lower temperatures, duplicate samples of 0.1 to 0.2 gram of each compound, ground to 50- to 80-mesh, were weighed into light-weight aluminum dishes, 55 mm. in inside diameter, 18 mm. deep, evenly distributed over the flat bottom, and placed in gently circulating air in a conditioned room at 24° C., 50% relative humidity, with an "umbrella" of paper over them to guard against possible falling dust. These were weighed at intervals of 10 to 20 days.

Results and Discussion

The solubilities of 5-propenyl guaethol at 24° C., read from the curves established as described, are given in Tables I and II. The values from these tables for 95% by volume ethanol and for 100% propylene glycol are in substantial agreement with those given by the manufacturer (*5*).

Solubilities of the four flavoring compounds in water, and of 5-propenyl guaethol in aqueous propylene glycol and in aqueous ethanol, from 0° to 50° C., read from the experimental curves, are given in Table III. The values for bourbonal, vanillin, and coumarin are in general agreement at most points with those given by the manufacturer (*4*), and the solubilities found for vanillin are within the rather wide range reported by Mange and Ehler.

Melting points and relative volatilities of the four compounds are given in Table IV. The samples used melted within the ranges given in the literature. Although the experimental work done on relative volatilities was rather limited, it appears that coumarin is somewhat more volatile than 5-propenyl guaethol over the temperature range investigated. Vanillin has substantially lower volatility than these, while bourbonal is slightly less volatile than vanillin. However, from the point of view of use as flavoring materials, the differences in volatility are probably not significant. This was confirmed experimentally in the course of the flavor studies cited (*1*).

Literature Cited

(1) Cartwright, L. C., and Kelley, P. H., *Food Technol.*, **6**, No. 9, 372–6 (1952).
(2) Hodgman, C. D., "Handbook of Chemistry and Physics," 33rd ed., pp. 1763–70, Cleveland, Ohio, Chemical Rubber Publishing Co., 1951.
(3) Mange, C. E., and Ehler, O., *Ind. Eng. Chem.*, **16**, 1258–60 (1924).
(4) Monsanto Chemical Co., "Something about the Senses," trade bulletin.
(5) Shulton, Inc., "Vanitrope Brand of Propenyl Guaethol," *Tech. Bull.* **5.**

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Nutritive Values and Digestibility Are Studied Instrumentally

COTTONSEED MEAL EXTRACTS
Electrophoretic Patterns of Buffer Extracts Of Different Nutritive Value

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