although accounting for only 38% of the variance, separated 10 of the 11 White Riesling wines (R) from the nine Chardonnays (C) and four French Colombards (F). Weighted >0.50 on PC I (Data Set II) were eight components, found in higher concentrations in R than C or F, some of which had fruity, floral descriptions, consistent with the aroma of R. Weighted <-0.50 on PC I were three "fruity" esters, also consistent with the characteristic aromas of C and F. Interestingly, linalool, often thought to be important in R, was not weighted heavily on PC I. By SDA, the 24 wines were sorted successfully into three variety categories by discriminant functions using five components.

Supplementary Material Available: Peak means (ppb) of triplicate analyses of each of the 24 wines are listed (15 pages). Ordering information is given on a current masthead page.

LITERATURE CITED

Bertuccioli, M., Montedoro, G., *J. Sci. Food Agric.* **25**, 675 (1974).
Bertuccioli, M., Montedoro, G., *Riv. Sci. Tech. Alim. Nutr. Um.* **5**, 39 (1975).
Bertuccioli, M., Viani, R., *J. Sci. Food Agric.* **27**, 1035 (1976).
Broschat, T., *HortScience* **14**, 114 (1979).
Coope, G. C., Masters Thesis, University of California, Davis, CA, 1977.
Dixon, W. J., Ed., Biomedical Computer Programs, University of California Press, Berkeley, CA, 1973.
Dixon, W. J., Brown, M. B., Ed., "Biomedical Computer Programs", P-Series, University of California Press, Berkeley, CA, 1977.
Flath, R. A., Forrey, R. R., King, A. D., Jr., *Am. J. Enol. Viticult.* **23**, 159 (1972).
Forrey, R. R., Flath, R. A., *J. Agric. Food Chem.* **22**, 496 (1974).
Kwan, W., Kowalski, B., *J. Food Sci.* **43**, 1320 (1978).
Noble, A. C., "Analysis of Food and Beverages, Headspace Techniques", Academic Press, New York, 1978, p 203-228.
Noble, A., Coope, G., Murakami, A., *J. Agric. Food Chem.* **27**, 450 (1979).
Rapp, A., Hastrich, H., *Vitis* **17**, 228 (1978).
Rapp, A., Hastrich, H., Engel, L., Knipser, W., "Flavor or Foods and Beverages", Academic Press, New York, 1978, p 391-417.
Schreier, P., Drawert. F., *Z. Lebensm.-Unters.-Forsch.* **154**, 27 (1974).
Schreier, P., Drawert, F., Junker, A., *Z. Lebensm.-Unters.-Forsch.* **154**, 279 (1974).
Schreier, P., Drawert, F., Junker, A., *Z. Lebensm.-Unters.-Forsch.* **157**, 34 (1975).
Schreier, P., Drawert, F., *Chem. Mikrobiol. Technol. Lebensm.* **4**, 154 (1976).
Schreier, P., Drawert, F., Junker, A., *Chem. Mikrobiol. Technol. Lebensm.* **5**, 45 (1977).
Schreier, P. Drawert, F., Junker, A., Reiner, L., *Mitt. Klosterneuburg* **26**, 225 (1976).
Siegmund, H., Bachmann, K., *Z. Lebensm.-Unters.-Forsch.* **166**, 298 (1978).
Simpson, R., *Chem. Ind. (London)*, 37 (1977).
Simpson, R., *Vitis* **17**, 274 (1978).
Simpson, R., Strauss, C., Williams, P. J., *Chem. Ind. (London)*, 663 (1977).
Spencer, M., Pangborn, R. M., Jennings, W. G., *J. Agric. Food Chem.* **26**, 725 (1978).
Stenroos, L. E., Siebert, K. J., Meilgaard, M. C., *J. Am. Soc. Brew. Chem.* **34**, 4 (1976).
Tassan, C., Russell, G. F., *J. Food Sci.* **39**, 64 (1974).
Thorndike, R. M., Correlational Procedures for Research, Gardner Press, Inc., New York, 1978.
van Wyk, C. J., Webb, A. D., Kepner, R. E., *J. Food Sci.* **32**, 660 (1967a).
van Wyk, C. J., Kepner, R. E., Webb, A. D., *J. Food Sci.* **32**, 664 (1967b).
van Wyk, C. J., Kepner, R. E., Webb, A. D., *J. Food Sci.* **32**, 669 (1967c).
von Sydow, E., Anderson, J., Anjon, K., Karlsson, G., *Lebensm.-Wiss. Technol.* **3**, 11 (1970).

Received for review August 8, 1979. Accepted November 9, 1979. Part of this paper was presented at the 175th National Meeting of the American Chemical Society, Division of Agriculture and Food Chemistry, Anaheim, California, March 1978.

Components of Almond Hulls: Possible Navel Orangeworm Attractants and Growth Inhibitors

Ron G. Buttery,* Edwin L. Soderstrom,[1] Richard M. Seifert, Louisa C. Ling, and William F. Haddon

A total of 44 components of the vacuum steam volatile oil of almond hulls have been identified using capillary GLC-MS. Major components include nonanoic acid, eugenol, (*E*)-2-decenal, benzaldehyde, nonanal, nonanol, and an unidentified lactone (mol wt 168). Unusual components include 6-methyl-3,5-heptadien-2-one, geranylacetone, borneol, γ-nonalactone, and methyleugenol. Direct ether extraction of the hulls gave 1-1.5% of a nonvolatile triterpenoid.

The navel orangeworm *Amyelois transitella* is a serious pest to the almond (*Prunus amygdalus*) crop in California (cf. Curtis and Barnes, 1977). The moth lays its eggs on the outside of the almond hull and the larva consumes some of the hull before finding its way into the kernel or completes its life cycle in the hull.

Previous work by one of the authors (Soderstrom, 1978) had indicated that there was some growth inhibition to the navel orangeworm with the Mission variety almond hulls relative to the Nonpareil variety. It seemed possible that this inhibition was due to the presence of some unknown chemical component in the Mission variety. The volatile chemical components are of interest also from another point of view in that they may be involved in the olfactory attraction of the navel orangeworm to the almond hulls.

Western Regional Research Laboratory, Science and Education Administration, Agricultural Research, U.S. Department of Agriculture, Berkeley, California 94710 (R.G.B., R.M.S., L.C.L., W.F.H.), and the Stored Product Insects Laboratory, Science and Education Administration, Agricultural Research, U.S. Department of Agriculture, Fresno, California 93727.

There seems to be very limited information on the chemical components of almond hulls in the literature. There is some information on the identities of the volatile chemical components of the almond kernel (Takei et al., 1974); Takei and Yamanishi, 1974). These are, however, concerned mostly with processed (roasted) forms of almond.

The present work concentrated on the identification of the volatile components of almond hulls in order that these compounds could be tested for their effectiveness in growth inhibition and also as olfactory attractants.

EXPERIMENTAL SECTION

Materials. Almond hulls (dry) were obtained from almond growers near Fresno, California. More than three different samples (from different farms) of each of the varieties, Mission and Nonpareil, were examined.

Authentic samples of chemical compounds were obtained from reliable commercial souces or synthesized by known methods. They were purified by gas–liquid chromatography (GLC) separation before use.

Isolation of Volatile Oil. Almond hulls (2.3 kg) were placed in a 12-L round-bottom flask together with 6 L of odor-free water. A Likens–Nickerson steam distillation continuous extraction head was attached to the flask. Purified hexane (100 mL) was placed in a flask attached to the solvent arm of the head. The isolation was carried out under reduced pressure (100 mm) for 3 h with the almond hulls at 45–50 °C. The condensor on the head was cooled with water–ethanol at 0 °C. After the isolation the hexane extract was dried by freezing out the water, filtered, and concentrated, using low hold up distillation columns, to give the almond hull volatile oil (ca. 90–120 mg). Exactly the same method was used for both Mission and Nonpareil varieties.

Extraction of Triterpenoids. Almond hulls (800 g, Mission variety) were ground to a coarse powder in a mortar and pestle, stirred for 30 min with ether (1 L) and water (100 mL). The slurry was then poured into an empty chromatography column (60 cm long × 7.5 cm o.d.) and washed with more ether (1 L). Removal of the solvent with a rotary evaporator gave 12.2 g of a white solid. The solid was washed with hexane (4 × 100 mL) to remove fats. It was recrystallized from ethyl acetate.

Capillary GLC–Mass Spectral (GLC–MS) Analysis. The main capillary GLC–MS analyses were carried out using a 150 m long × 0.64 mm i.d. Pyrex glass capillary column coated with Carbowax 20-M (containing 5% Igepal CO-880). Other capillary GLC–MS analyses were also carried out using Pyrex glass capillary GLC columns of similar dimensions to the above, but one was coated with Silicon SF (96) and another with Tween 20. For the main capillary GLC–MS analysis using the Carbowax 20-M column, the column was held at 50 °C constant for the first 30 min after the injection and then programmed at 1 °C/min from 50 to 170 °C and held at this upper limit. The column inlet pressure was 16 psi He. A single stage Lewellyn–Littlejohn silicon rubber membrane separator was used to couple the capillary GLC column to the mass spectrometer (a modified Consolidated 21-620 cycloidal type). Electron ionization voltage was 70 V.

Packed Column GLC–Infrared Spectral (IR) Analysis. Components were separated from the almond hull volatile oil using a 3 m long × 0.64 cm o.d. stainless steel column packed with 80–100 mesh Chromosorb G-DMCS coated with 2% Carbowax 20-M. The column was programmed at 2 °C/min from 50 to 170 °C. Samples were collected in dry ice cooled Pyrex tubes (3 mm o.d. × 14 cm long). IR spectra were measured as thin films between ultramicro salt plates or as solutions in CS_2 using an ultramicro cavity cell and a reflecting beam condensor with a Perkin Elmer Model 237 instrument.

Table I. Compounds Identified in the Vacuum Steam Volatile Oils of Nonpareil and Mission Variety Almond Hulls

compounds identified[a,c]	Nonpareil, %	Mission, %
alkanals		
(3) hexanal	0.7	0.6
(11) heptanal	0.3	0.3
(24) octanal	0.4	0.3
(34) nonanal[b]	4	7
(54) decanal[d]	ca. 1	ca. 1
(71) undecanal	0.2	0.2
(122) tetradecanal	<0.1	<0.1
2-alkenals		
(15) (*E*)-2-hexenal	0.3	0.2
(28) (*E*)-2-heptenal	2	1
(57) (*E*)-2-nonenal	1	0.7
(74) (*E*)-2-decenal[b]	7	3
(91) (*E*)-2-undecenal	0.3	0.2
2,4-alkadienals		
(46) (*E,Z*)-2,4-heptadienal	0.2	0.9
(50) (*E,E*)-2,4-heptadienal[b]	1	3
(80) (*E,E*)-2,4-nonadienal[d]	ca. 0.1	ca. 0.1
(92) (*E,Z*)-2,4-decadienal[b]	0.3	0.9
(97) (*E,E*)-2,4-decadienal[b]	1	3
alkanols		
(32) hexanol	1	1
(47) heptanol	0.7	0.9
(61) octanol[d]	ca. 2	ca. 2
(77) nonanol	4	2
terpenoids		
(30) 6-methyl-5-hepten-2-one	0.2	1
(65) 6-methyl-3,5-heptadien-2-one	0.4	1
(60) linalool	0.1	0.1
(80) borneol[d]	ca. 0.7	ca. 4
(111) geranylacetone	0.6	0.4
(105) α-ionone[d]	ca. 0.1	ca. 0.2
(121) β-ionone	0.1	0.4
aromatic		
(54) benzaldehyde[b]	6	12
(75) phenylacetaldehyde	1	0.3
(84) *p*-methylacetophenone[d]	ca. 0.1	ca. 0.3
(90) methyl salicylate	0.4	0.7
(98) 2-methylnaphthalene	0.1	0.1
(105) guaiacol	3	0.5
(115) 2-phenylethanol	0.9	1
(130) methyleugenol	1	0.1
(143) eugenol[b]	8	0.9
furans		
(16) 2-pentylfuran	0.9	0.2
(45) furfural[d]	ca. 2	ca. 4
(61) 5-methylfurfural[d]	ca. 2	ca. 2
others		
(45) 1-octen-3-ol[d]	ca. 0.5	ca. 1
(56) (*E,E*)-3,5-octadien-2-one	0.1	0.4
(132) γ-nonalactone	0.6	0.3
(135) octanoic acid	3	2
(144) nonanoic acid	10	5

[a] Mass spectrum and GLC retention data of all compounds listed consistent with that of authentic samples. [b] Infrared spectrum consistent with that of an authentic sample in addition to footnote *a*. [c] Peak numbers corresponding to the peaks in Figure 1 are shown in parentheses immediately before the compound name. [d] Multicomponent peak, no accurate quantitative analysis possible.

RESULTS AND DISCUSSION

Several samples, using both Mission and Nonpareil varieties, were studied. The volatile oil, obtained by vacuum steam distillation continuous extraction amounted to ca. 40–50 parts per million (ppm) of the hulls. The main

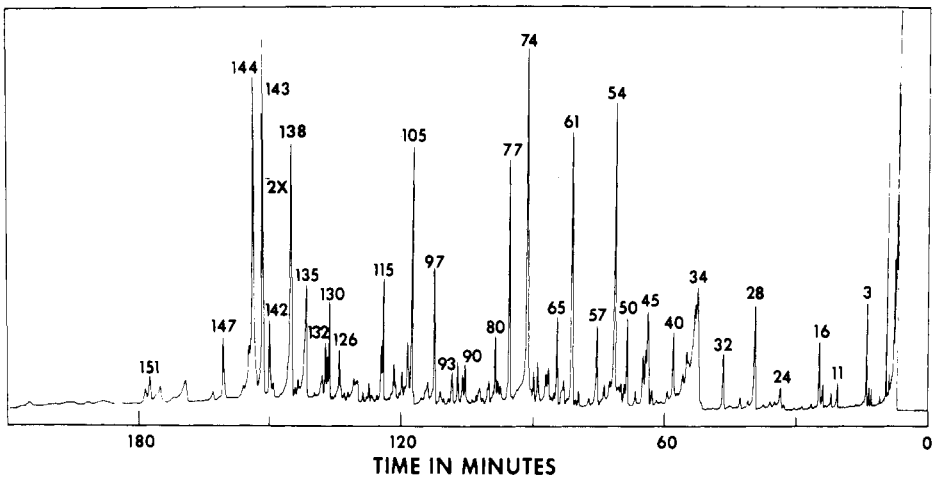

Figure 1. Capillary GLC analysis of the vacuum steam volatile oil from Nonpareil variety almond hulls. For GLC conditions see text.

analysis was carried out using capillary GLC–MS. Confirmatory information was also obtained by packed column GLC separation followed by infrared (IR) spectral analysis.

Table I lists the compounds identified together with the approximate relative percentage of the component found in the volatile oil for both Mission and Nonpareil varieties. There is some variation with different samples and the quantitative figures are only meant to give a general idea of what might be considered to be fairly typical sample.

The major components in the Nonpareil variety volatile oil include nonanoic acid (10%), eugenol (8%), (*E*)-2-decenal (7%), benzaldehyde (6%), nonanal (4%), nonanol (4%), and an unidentified lactone, mol wt 168 (6%). These components also seem to be prominent in the Mission variety except for eugenol which is considerably less. It is interesting that the C_9 straight chain aliphatic acid, aldehyde, and alcohol are among the major components in both varieties. The almond kernel has a high concentration of oleic acid (Beuchat and Worthington, 1978). The lipids in almond hulls do not appear to have been studied but if oleic acid is also a predominant fatty acid in almond hull lipids, cleavage of the oleic acid double bond could lead to C_9 fragments. Decomposition of autoxidized oleic acid glyceride is known (Kimoto and Gaddis, 1974) to give predominately nonanal.

The presence of benzaldehyde in almond hulls was expected because it has been known to be present in almonds for many years and is widely used as an almond flavor. Its presence has been attributed to the amygdalin content of almonds (cf. Noller, 1957).

The alkanals, alkenals, alkadienals, and alkanols are qualitatively similar to those found in many vegetable materials. Their relative quantitative amounts are somewhat unusual, however, especially in regard to the relatively high concentrations of nonanal and (*E*)-2-decenal.

The most unique component found was an unidentified lactone (6% in Nonpareil, 10% in Mission) which is peak 138 in Figure 1. Its mass Spectrum (two most intense ions each 14 mass units above *m/e* 34, intensities in parentheses, molecular ion in dark type) showed 41 (89), 43 (98); 53 (32), 55 (46); 67 (26), 69 (28); 81 (20), 82 (13); 95 (19), 98 (31); 111 (7), 112 (6); 123 (13), 126 (100); 139 (9), 140 (14); 151 (2), 153 (4); **168** (4), 169 (0.6).

An infrared spectrum of peak 138 showed a carbonyl absorption at 5.65 μ indicating a lactone. A ^1H NMR spectrum showed no olefinic protons, a possible methyl group on a double bond (δ 2.07 ppm, s, 3 H), and a probable methyl group at the end of an aliphatic chain (δ 0.88 ppm, t, 3 H). Other features of the spectrum were more ambiguous. The *m/e* 126 ion in the mass spectrum corresponds to a loss of 42 mass units, indicating a butyl group (McLafferty rearrangement). From the data it was thought that 5-methyl-6-butyl-3,4-dihydro-2-pyrone was a possible structure. However, synthesis of this compound and measurement of its spectra showed it to be different from our unknown. Further studies are intended in the future to isolate more of peak 138 and obtain additional spectral and chemical data.

Methyleugenol is a known, very effective, attractant (Steiner, 1952) for another insect, the oriental fruitfly (*Dacus dorsalis*). It is interesting that it occurs in almond hulls which are essentially a fruit tissue. This compound does not appear to have been tested with the navel orangeworm.

Tests with the Navel Orangeworm. The compounds nonanal, benzaldehyde, hexanal, and (*E*)-2-hexenal were tested for attraction and for their effect in the diet of the navel orangeworm. These compounds did not prove effective as attractants or as growth inhibitors.

Further studies are intended in this area.

Volatiles Common to Almond Hulls and Oranges. As the navel orangeworm (as its name implies) sometimes infests oranges as well as almond hulls, it might be of some use to consider volatiles common to both fruits. The volatiles of oranges have been fairly thoroughly studied (Teranishi et al., 1966; Schultz et al., 1971). Nonanal is a major component of the almond hulls. The close homologues octanal and decanal are major components of orange volatiles although nonanal itself seems to be absent. The only other component occurring in reasonable amounts that seems to be common to both orange and almond hulls is hexanol.

Triterpenoid Components. Direct extraction of the almond hulls with diethyl ether gave a white solid (1–1.5% of the hulls). This solid was insoluble in hexane and was purified from ether-soluble fats and oil by washing with hexane. It was then recrystallized from ethyl acetate and had mp 250–255 °C. High-resolution mass spectra showed a molecular weight of 456.3604 which corresponds to the empirical formula $C_{30}H_{48}O_3$. The mass spectral pattern and infrared spectrum were quite similar to that of the triterpenoid oleanolic acid . There were some differences, however, and the almond hull triterpenoid appears to have a slightly different structure from oleanolic acid although further research is intended to determine this with more certainty. Some triterpenoids are known to be insect feeding inhibitors (Warthen, 1979), and it is possible that

the triterpenoids in almond hulls are important in considering the resistance of different almond varieties to the navel orangeworm.

LITERATURE CITED

Beuchat, L. R., Worthington, R. E., *J. Food Technol.* **13**, 355 (1978).
Curtis, R. K., Barnes, M. M., *J. Econ. Entomol.* **70**, 395 (1977).
Kimoto, W. I., Gaddis, A. M., *J. Am. Oil Chem. Soc.* **51**, 307 (1974).
Noller, C. R. "Chemistry of Organic Compounds", W. B. Saunders Co., Philadelphia, (1957), p 255.
Schultz, T. H., Flath, R. A., Mon, T. R., *J. Agric. Food Chem.* **19**, 1060 (1971).
Soderstrom, E. L., USDA, Fresno, CA, unpublished work, 1978.
Steiner, L. F., *J. Econ. Entomol.* **45**, 241 (1952).
Takei, Y., Shimada, K., Watanabe, S., Yamanishi, T., *Agric. Biol. Chem. (Jpn.)* **38**, 645 (1974).
Takei, Y., Yamanishi, T., *Agric. Biol. Chem. (Jpn.)* **38**, 2329 (1974).
Teranishi, R., Lundin, R. E., McFadden, W. H., Mon, T. R., Schultz, T. H., Stevens, K. L., Wasserman, J., *J. Agric. Food Chem.* **14**, 447 (1966).
Warthen, J. D. Science and Education Administration, Agricultural Reviews and Manuals, Northeastern Series, No. 4, April 1979.

Received for review July 13, 1979. Accepted October 1, 1979.

Pattern Recognition Analysis of Gas Chromatographic Data. Geographic Classification of Wines of *Vitis vinifera* cv. Pinot Noir from France and the United States

Wing-On Kwan and Bruce R. Kowalski*

Organic compositions of 40 wines of *Vitis vinifera* cv. Pinot Noir from France and the United States were analyzed by glass capillary gas chromatography. Classifications of these wines according to their geographic origins were achieved by applying pattern recognition techniques to the chemical data. Key components for the classifications were then identified by gas chromatography–mass spectrometry. Two neutral compounds, 1-hexanol and cyclohexane, were found to be most important for the classification of French and American Pinot Noirs, while *p*-hydroxybenzaldehyde and 2-phenylethanol were major components for distinguishing California Pinot Noirs from those produced in the Pacific Northwest region.

The use of conventional gas chromatography has allowed the identification of many volatile components in wine (Amerine, 1954; Webb and Muller, 1972). Latest advances in glass capillary gas chromatography enable even finer separation of components in such a complex mixture, but to identify every volatile component can be a tiresome, and in some cases, unnecessary task. The best approach is to identify only those components which are related to the specific properties of wine and then make the identification. Before this can be achieved, relevant information must be ferreted out from a massive amount of gas chromatographic data. Pattern recognition techniques, which have been proven successful in enological research (Kwan and Kowalski, 1978; Kwan et al., 1979), are suited to this type of multivariate analysis.

Volatile constituents of many varieties of *Vitis vinifera* have been studied (Webb and Noble, 1976; Sakato et al., 1975; Brander, 1974; Webb et al., 1969; Van Wyk et al., 1967), but rarely were attempts made to correlate these organic profiles to various properties of the wine. In this study, volatile constituents of wines of *Vitis vinifera* cv. Pinot Noir from France and the United States were analyzed by glass capillary gas chromatography. Pattern recognition techniques were then used to analyze these data. Key components which related to the geographic origins of the wine samples were selected. Identification of these key components were achieved with the use of gas chromatography–mass spectrometry.

Laboratory for Chemometrics, Chemistry Department, University of Washington, Seattle, Washington 98195.

EXPERIMENTAL SECTION

Description of the 40 wines of *Vitis vinifera* cv. Pinot Noir from France and the United States is given in Table I.

Organic Component Extraction. Two hundred milliliters of Pinot Noir wine was extracted with 500 mL of methylene chloride in a separatory funnel. The emulsion which formed upon vigorous agitation of wine and solvent was broken down by centrifugation. Free acids in the wine extract were separated by extraction with 100 mL of 5% Na_2CO_3 solution. The aqueous phase was back-extracted with 100 mL of methylene chloride to recover nonacidic components. The back extract was combined with the bulk of the "neutral" fraction and dried over anhydrous Na_2SO_4. The combined neutral fraction was then concentrated to 2 mL by rotary evaporation at 0 °C and stored in a vial for gas chromatographic analysis.

The pH of the Na_2CO_3 solution containing organic acids was adjusted to a value of 1.0 by adding 6 N H_2SO_4. The organic acids were then separated from the aqueous solution by extracting with 200 mL of diethyl ether. The ether phase was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation to a volume of 2 mL at 0 °C, which was then stored in a vial for future gas chromatographic analysis.

Gas Chromatographic Analysis. A Hewlett-Packard 5840A gas chromatograph with a flame ionization detector was used. The instrument was fitted with a 30-m SE-30 glass capillary column having an inner diameter of 0.25

0021-8561/80/1428-0356$01.00/0