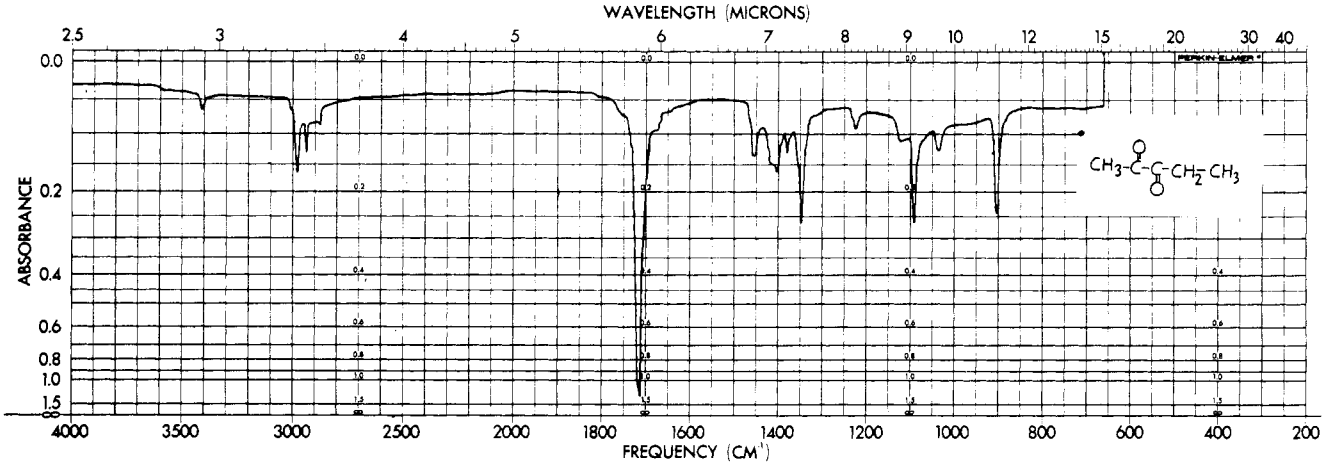

Figure 3. Ir spectrum of 2,3-pentanedione in CCl_4.

Table II. Nmr Spectrum of 3-Hydroxy-3-penten-2-one (60 MHz, CCl_4)

Peaks at ppm (δ)	Assignments
1.5 (d)	CH_3 adjacent to a –C=C– group
2.0 (s)	CH_3 adjacent to a C=O group
5.0 (s)	OH
6.1 (q)	–C=C–

characteristic of unenolized 2,3-pentanedione (Figure 3) and indicate reversal of the enol in the 20–30 min needed for transfer and spectral scanning. These two bands are absent in the spectrum of the pure enol Me_3Si ether (Figure 2). The appearance of 1130- (s) and 870-cm^{-1} (ms) bands in Figure 2 is due to C–O–Si asymmetric stretching and Si–C stretching, respectively, of the trimethylsilyl ether group. The disappearance of the bonded OH band is obviously due to the conversion of the hydroxy to the Me_3Si ether.

The structure of the enol form was confirmed by nmr. The peak assignments in its nmr spectrum are given in Table II. The mass spectrum of the enol Me_3Si ether showed the typical pattern of a silyl compound with a molecular ion of m/e^+ 172, and a large fragment ion of m/e^+ 157 (P – 15). The Me_3Si ether formation proves the existence of an enol group. In the uv region, 2,3-pentanedione exhibits an absorption band at λ_{max}(EtOH) 265 mμ, while the enol form shifted to 255 mμ. The buttery caramel aroma compound gives a bluish purple color with ferric chloride, indicating the presence of an enol, while 2,3-pentanedione produces no color with this reagent. The presence of a caramel aroma is probably attributed to the planar C(=O)C(—OH)=C—C grouping in this compound (Hodge, 1967).

In view of the fact that both 2,3-pentanedione and 2,4-pentanedione enolize to a significant extent and 2,3-butanedione does not, it appears that aliphatic diketones containing a CH_2 group adjacent to one of the carbonyl groups, but not necessarily between the two, may be enolized.

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Volatile Components of *Prunus salicina*, Var. Santa Rosa

Ralph R. Forrey and Robert A. Flath*

The volatile components of Santa Rosa plum were concentrated by vacuum co-distillation with water followed by solvent extraction of the distillate. The concentrate was then examined by gas chromatography–mass spectrometry. Fifty-three components of the concentrate were identified.

The Santa Rosa plum (*Prunus salicina*, formerly *Prunus triflora*) is a type of Japanese plum. The species is probably a native of China, but was introduced into California from Japan around 1870 (Bailey, 1941). The Santa Rosa variety was originated by Luther Burbank and was first offered by a commercial nursery in 1907 (Hedrick, 1911). The fruit of the Santa Rosa plum is large (~5–6 cm diameter) and has a dark purplish crimson skin, with flesh

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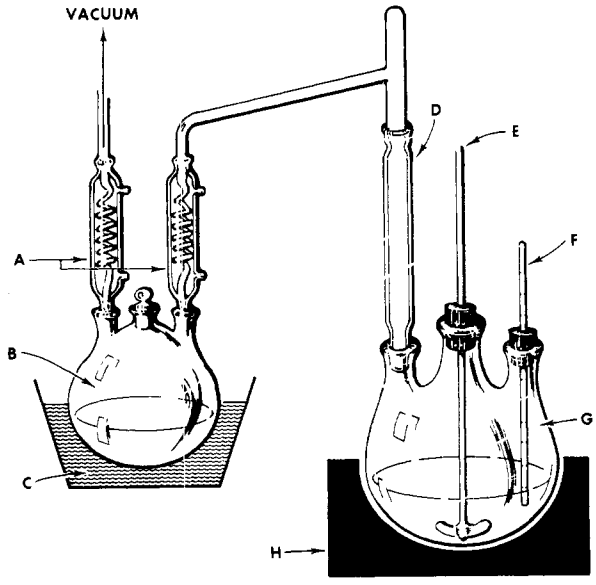

Figure 1. Aroma concentration apparatus: (A) double-wall condensors cooled with recirculated water at 0–2°; (B) distillate collection flask; (C) solid carbon dioxide–isopropyl alcohol bath; (D) insulated extension tube; (E) glass–Teflon stirrer; (F) thermometer; (G) 5-l. flask containing fruit starting material; (H) heating mantle.

ranging in color from deep red to pale yellow-amber with increasing distance from the skin. It is very popular in the fresh fruit market because of its distinctive flavor.

EXPERIMENTAL SECTION

Concentrate Preparation. Fresh fruit was purchased from a wholesale market. The fruit was gently rinsed with water, dried, and sorted by hand to select sound fully ripe fruit. A quantity of this fruit was cut into small slices and the seeds discarded. The cut fruit (3.91 kg) was placed in a 5-l. round-bottomed flask set up as shown in Figure 1. Distilled water (0.75 l.) and antifoam agent (0.5 g, Dow Corning Antifoam AF Emulsion) were added to the flask contents. The stirred mixture was heated to boiling (33°) for 3 hr at a pressure of 37 mm, and the distillate (1.2 l.) was collected in a solid carbon dioxide–isopropyl alcohol cooled receiver. The frozen distillate was subsequently melted, saturated with sodium chloride, and extracted with diethyl ether (three 50-ml portions). Most of the solvent was stripped from the solution by distillation through a short Raschig ring-packed column, leaving 1 ml of yellow solution. One-half of this residue was further concentrated under a slow stream of nitrogen and used for gas chromatographic–mass spectral examination.

Component Separation and Identification. The equipment and techniques used in this study are similar to those used in previous flavor investigations conducted in our laboratory (Flath *et al.*, 1969; Flath and Forrey, 1970). Gas chromatographic separations were carried out with a 900 ft × 0.03 in. i.d. stainless steel open-tubular column coated with methyl silicone oil (General Electric SF 96(50)) containing 5% Igepal CO-880. The column was mounted in a modified Beckman Thermotrac oven fitted with a Carle dual thermistor detector. For gc–mass spectral examinations the detector effluent was passed through a membrane type interface (Black *et al.*, 1969; 0.001-in. thick methyl silicone membrane; 0.5 in.^{2} area) into an Electronic Associates Quad 300 quadrupole mass spectrometer. The gas chromatographic column oven was programmed from 48 to 185° at a rate of approximately 1.5°/min. Mass spectra were recorded as desired with an oscillographic recorder at scan rates of 1 or 1.5 sec. Individual components were identified by comparing the plum component's mass spectrum with that of an authentic reference compound. These reference mass spectra were obtained with the same mass spectrometer used for the gc–mass spectral runs. The identity assignments were then verified by checking the gc relative retention behavior of the authentic samples on the open-tubular column when coinjected with the total plum aroma concentrate.

RESULTS AND DISCUSSION

A literature survey uncovered very little published information on plum volatiles. Villforth (1943) extracted plums with ether and pentane, but reported no compositional data.

The plum components identified in this study are listed in Table I; the position of each of these components in a gas chromatographic separation (Figure 2) is indicated by number. Inasmuch as the individual components were not isolated and rigorously identified, there is always some small degree of uncertainty in the assignment of a unique structure to a compound when the only data available are a low-resolution mass spectrum and a gc relative retention time comparison. This degree of uncertainty is much smaller with lower molecular weight components than with the higher molecular weight constituents. As higher molecular weight compounds are encountered, the sensi-

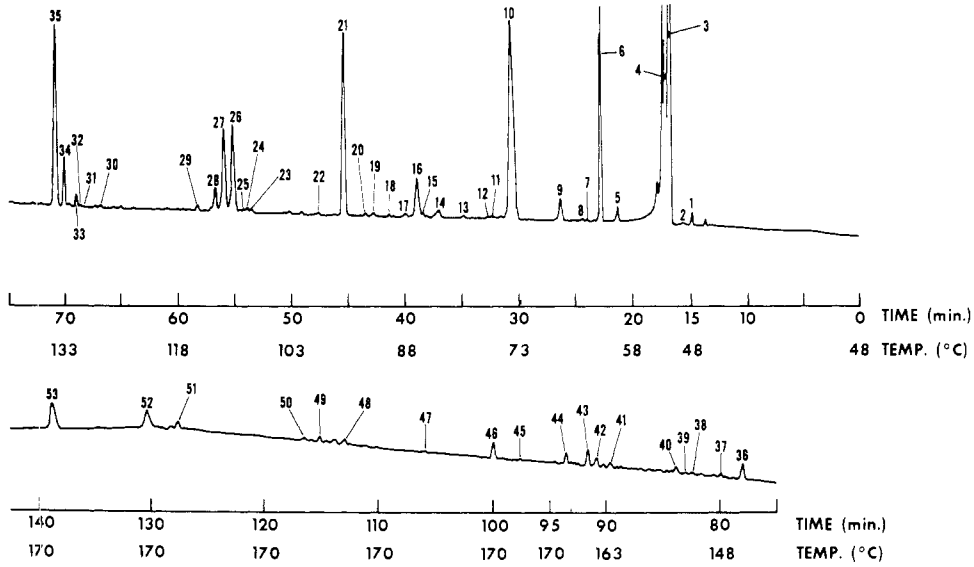

Figure 2. Gas chromatogram of Santa Rosa plum volatiles; 900 ft × 0.03 in. i.d. column coated with methyl silicone oil; dual thermistor detector.

Table I. Santa Rosa Plum Components

1. Acetaldehyde	19. 1-Pentanol	37. 1-Octanol
2. Methanol	20. Ethyl butyrate	38. 1-Heptyl acetate
3. Ethanol	21. 1-Butyl acetate	39. Linalool
4. Ethyl ether (solvent)	22. 2-Methyl-2-pentenal	40. Benzyl alcohol
5. 1-Propanol	23. 3-Methyl-1-butyl acetate	41. Benzyl acetate
6. Ethyl acetate	24. 2-Methyl-1-butyl acetate	42. 2-Phenylethanol
7. Chloroform	25. *trans*-3-Hexen-1-ol	43. Ethyl octanoate
8. 2-Methyl-3-buten-2-ol	26. *cis*-3-Hexen-1-ol	44. α-Terpineol
9. 2-Methyl-1-propanol	27. 1-Hexanol	45. Ethyl phenylacetate
10. 1-Butanol	28. *trans*-2-Hexen-1-ol	46. γ-Octalactone
11. 1-Penten-3-ol	29. 1-Pentyl acetate	47. 1-Methylnaphthalene
12. 1-Propyl acetate	30. Benzaldehyde	48. γ-Nonalactone
13. 1,1-Diethoxyethane	31. 1-Heptanol	49. Ethyl decanoate
14. 3-Hydroxy-2-butanone	32. 1-Butyl butyrate	50. Biphenyl
15. 3-Methyl-1-butanol	33. Ethyl hexanoate	51. Ethyl anisate
16. 2-Methyl-1-butanol	34. *cis*-3-Hexenyl acetate	52. γ-Decalactone
17. 2-Methyl-1-propyl acetate	35. 1-Hexyl acetate	53. Butylated hydroxytoluene
18. Diethyl carbonate	36. γ-Hexalactone	

tivity of each data source to small isomeric differences decreases in general, and the possibility of error increases. In all cases listed in Table I, the mass spectral and relative retention time data are fully consistent with the assignments made.

Most of the compounds found are fairly common fruit volatiles, with the possible exception of ethyl anisate. Acetate esters predominate, but appreciable quantities of the higher γ-lactones appear as well. Chloroform is used in our laboratory for syringe cleaning, so it is likely an artifact. Similarly, butylated hydroxytoluene is a preservative in the ether solvent used, so it is not a plum constituent.

Some effort was made to correlate the presence of certain components with the fruit's characteristic aroma. The gc column effluent was sniffed (thermistor detector), impressions of several judges were noted, and a number of test mixtures were subsequently prepared, using the gc chromatogram as a guide to the relative concentrations of the components. However, because of the seasonal nature of plums, fresh fruit material was not available for more formal and systematic evaluation of the components' aroma contributions.

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Autoxidation of Some Constituents of Hops. I. The Monoterpene Hydrocarbon, Myrcene

Robert H. Dieckmann and S. Rao Palamand*

Controlled degradation of myrcene, the major monoterpene hydrocarbon of hop oil, is discussed with special emphasis on the role of myrcene as a precursor for the formation of flavor compounds occurring in naturally aging hop oil. Products are isolated and identified by means of gas chromatographic, mass spectral, and infrared analyses. Related possible degradation pathways are suggested for a number of these second- and third-order terpenoid constituents, and spectral data for several terpene alcohols, oxides, ketones, and polymerization products are reported.

The study of the essential oil of hops (0.5–1.0% w/w) has been of importance to the brewing industry for many years, as hops constitute one of the major raw materials involved in the brewing cycle, contributing to both the odor and flavor of the finished beer. Only in the last 15 years, however, has gas chromatography, and later, mass spectrometry, given the analyst a tool which is capable of separating and analyzing the complex mixture of over 200 compounds. Results have been published by, among others, Buttery *et al.* (1964), Jahnsen (1963), and Roberts (1962). Of this mixture the main components of the fresh oil were found to be terpene hydrocarbons, specifically the monoterpene myrcene, and the sesquiterpenes β-caryophyllene and humulene (Buttery and Ling, 1967; Jahnsen, 1963).

Upon storage, however, DeMets and Verzele (1968) and Kowaka and Hashimoto (1967) reported that the oxygenated fraction of the oil shows a rapid build-up, with a concomitant loss of myrcene.

The purpose of this study, therefore, is to determine what changes are produced by short storage at elevated temperatures in a number of these hop oil components. Our experimental findings are presented for the first of these compounds, the monoterpene, myrcene.

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