either the salt-treated or untreated powders of the lyophilized diffusates. As already indicated, however, both aldoses and free amino groups were present in the lyophilized diffusates (Table II). Thus, a system conducive to development of browning existed in both the salt-treated and untreated diffusates. This supports the work of Tonsbeek et al. (1968), who detected two furanone derivatives and concluded that they resulted from the browning reaction and may contribute to the aroma of beef broth.

LITERATURE CITED

Batzer, O. F., Santoro, A. T., Landmann, W. A., J. Agr. Food Chem. 10, 94 (1962).
Batzer, O. F., Santoro, A. T., Landmann, W. A., Schweigert, B. S., J. Agr. Food Chem. 8, 498 (1960).
Bender, A. E., Wood, T., Palgrave, J. A., J. Sci. Food Agr. 9, 812 (1958).
Blackburn, S., "Analytical Methods of Protein Chemistry," Vol. 4, Pergamon Press, New York, N. Y., 1966, p 89.
Florkin, H., Stolz, E. H., Compr. Biochem. 7, 73 (1963).
Leach, S. J., "Analytical Methods of Protein Chemistry," Pergamon Press, New York, N. Y., 1966, p 3.
Lento, H. G., Ford, J. A., Denton, A. E., J. Food Sci. 29, 435 (1964).
Mabrouk, A. F., Jarboe, J. K., O'Connor, E. M., J. Agr. Food Chem. 17, 5 (1969).
Macy, R. L., Naumann, H. D., Bailey, M. E., J. Food Sci. 29, 136 (1964).
Müller, G., Deut. Z. Verdau.-Stoffwechselkr. 25, 77 (1965).
Müller, G., Anal. Abstr. 14, 1559 (1967).
Pepper, F. H., Pearson, A. M., J. Food Sci. 34, 10 (1969).
Pepper, F. H., Pearson, A. M. J. Agr. Food Chem. 19, 964 (1971).
Randerath, K., "Thin-Layer Chromatography," Academic Press, New York, N. Y., 1966.
Smith, I., "Chromatographic and Electrophoretic Techniques," Vol. 1, Interscience, New York, N. Y., 1960, p 60.
Spark, A. A., J. Sci. Food Agr. 20, 308 (1969).
Tonsbeek, C. H. T., Plancken. A. J., v. d. Weerdhof, T., J. Agr. Food Chem. 16, 1016 (1968).
Wasserman, A. E., Gray, N., J. Food Sci. 30, 801 (1965).
Zaika, L. L., Wasserman, A. E., Monk, C. A., Jr., Salay, J., J. Food Sci. 33, 53 (1968).

A New Caramel Compound from Coffee

Jo-Fen T. Kung

A pleasant, buttery caramel aroma from a coffee aroma concentrate has been identified as the enol form of 2,3-pentanedione, 3-hydroxy-3-penten-2-one. The enol was also produced by injecting 2,3-pentanedione into a gas chromatograph with a high injection port temperature (300° or higher). The unknown was trapped and identified by ir and nmr. The enol could be stabilized as its trimethylsilyl ether and its structure was further confirmed by mass spectrometry.

During a gas chromatographic fractionation of a coffee aroma concentrate, a particularly pleasant and desirable coffee-caramel aroma was isolated. This was identified by mass spectrometry as 2,3-pentanedione. However, the ir and nmr spectra indicated that this compound was more likely the enol form of the α-diketone.

Numerous reports appear in the literature on the studies of keto-enol tautomerism of carbonyl compounds, triacylmethanes, and cyclodiketones (Koltsov and Kheifets, 1971). Gerbier (1962) compared the enolization of 2,4-pentanedione, 2,5-hexanedione, and 2,3-butanedione as the pure liquid, dilute CCl_4 solutions, and vapor states. He found that enolization occurred in all three states for 2,4-pentanedione, and was complete in the vapor state, although only one C=O group was enolized in each molecule. This evidence was not as clear for 2,5-hexanedione. From this evidence he concluded that the H atom participating in enolization came from a CH_2 group situated between the two C=O groups.

Schwarzenback and Wittwer (1947) reported 2,3-butanedione to be enolized in the pure state, to the extent of 0.0056%. Except for this report, there have been no reports on the enolization of aliphatic α-diketones.

EXPERIMENTAL SECTION

Preparation of 3-Hydroxy-3-penten-2-one. Portions (100 mg) of redistilled 2,3-pentanedione were injected into a Perkin-Elmer Model 800 gas chromatograph, with a flame-ionization detector and effluent splitter, and dual

Technical Center, General Foods Corporation, Tarrytown, New York 10591.

stainless steel columns ($\frac{1}{8}$ in. × 6 ft) packed with 15% OV-101 on Anakrom ABS, 80-90 mesh size. The operating conditions were as follows: injection port temperature, 300-350°; column temperature, 4 min at 70°, then programmed to 300° at 5°/min; detector temperature, 300°; helium flow rate, 30 ml/min; hydrogen, 30 psi; and air flow rate, 360 ml/min. The injection port temperature had to be maintained at 300-350° in order to facilitate enolization. The component eluted at 3.5 min contained mainly the enol form and had a buttery caramel aroma. It was collected into a melting point tube cooled with Dry Ice. The collected material was dissolved in a small amount of Freon 113 and the enol form was purified by rechromatography of the Freon solution on a Perkin-Elmer Model 900 gas chromatograph, with a flame ionization detector and effluent splitter, and dual stainless steel columns ($\frac{1}{8}$ in. × 6 ft) packed with 15% stabilized DEGS on Anakrom ABS, 80-90 mesh size. The operating conditions were as follows: injection port temperature, 180°; column temperature, 50-175° at 2.5°/min; detector temperature, 180°; helium flow rate, 17 ml/min; hydrogen, 22 psi; air flow rate, 54 psi. The injection port temperature was kept at 175-180° in order to prevent thermal degradation of the enol form at higher temperatures. The pure enol (R_t of 12.9 min) was trapped into a melting point tube as described above. The unenolized 2,3-pentanedione was eluted at 5.8 min.

2,3-Pentanedione can also be enolized at a lower temperature in the presence of an acid. It was mixed with hydrochloric acid in a ratio of 2:1 in a closed vial and heated at 110° for 1 hr. After being cooled to room temperature, the mixture was extracted with Freon 113. The enol form
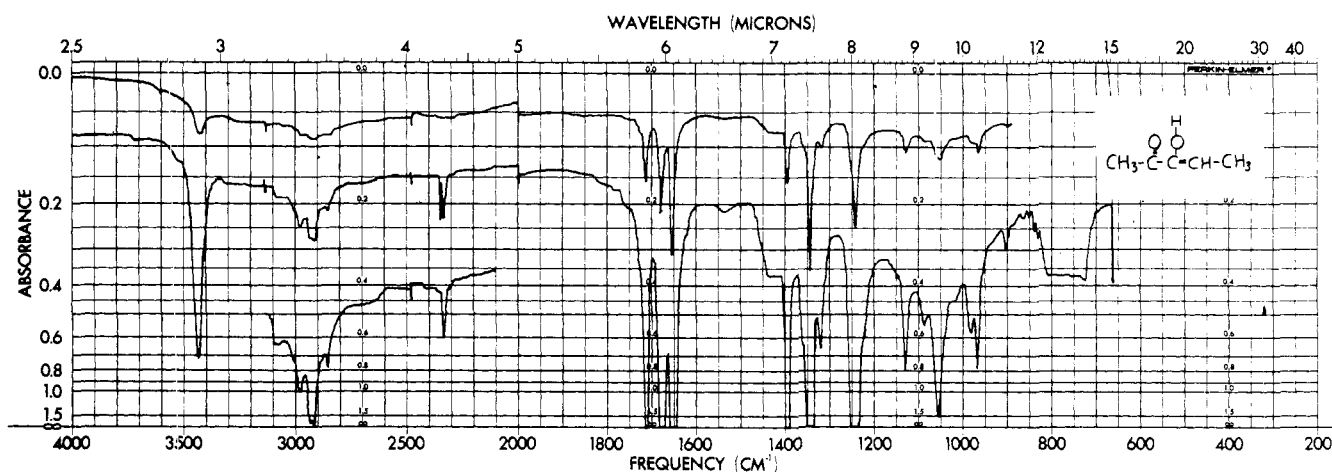
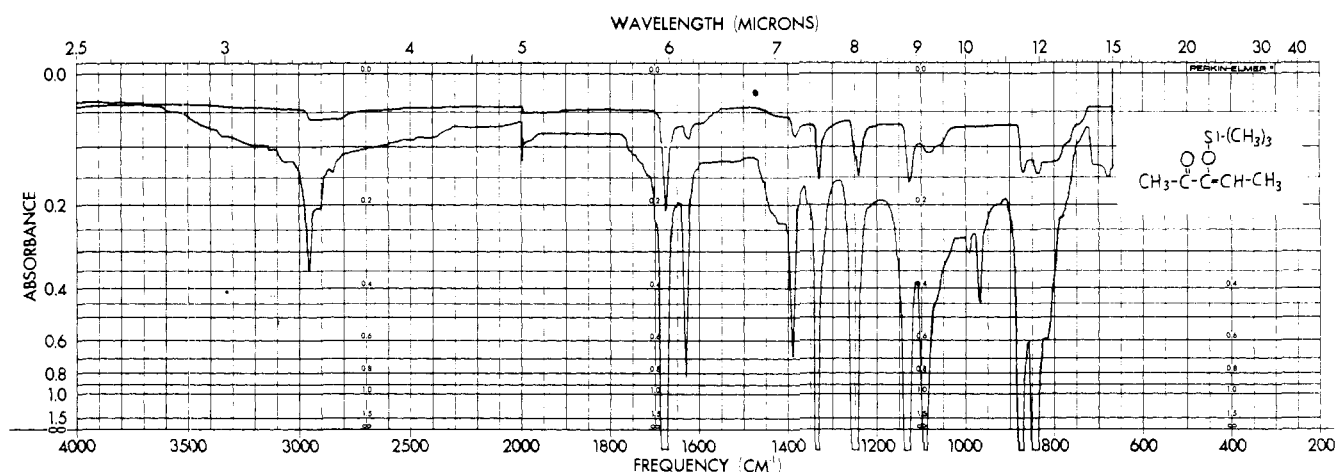Figure 1. Ir spectrum of a 3-hydroxy-3-penten-2-one and 2,3-pentanedione mixture in CCl₄.

Figure 2. Ir spectrum of the Me₃Si ether of 3-hydroxy-3-penten-2-one in CCl₄.

in the extract was then isolated by gas chromatography (gc) using the P-E 900 with a DEGS column as described above.

Preparation of the Trimethylsilyl Ether of the Enol Form. The pure 3-hydroxy-3-penten-2-one was converted to its silyl ether with hexamethyldisilazane and trimethylchlorosilane immediately after gc isolation. The silyl ether was then separated from the excess reagents by chromatographing on the P-E 900 with a 15% DEGS column. It had a retention time of 10.7 min under the conditions previously described.

RESULTS AND DISCUSSION

In the course of studies on coffee aroma, a very pleasant buttery caramel aroma was noted in the effluent of our gas chromatograph. Mass spectrometry gave evidence for an identification as 2,3-pentanedione. The odor and gc retention time did not support this identification. More extensive studies were, therefore, undertaken to identify this very desirable aroma compound.

The material was trapped and an infrared spectrum obtained (Figure 1). This gave evidence for the existence of a hydroxy group, a -C=C-, an α,β-unsaturated carbonyl, and an α-diketone. When it was found that this new material could be produced in the gas chromatograph by injecting 2,3-pentanedione at a high injection port temperature (300°), the existence of the enol form, 3-hydroxy-3-penten-2-one, was postulated. This method was used to produce the material used for the confirmation of its structure. Enolization also took place in the presence of concentrated acid at 110°, as described in the Experimental Section.

Table I. Ir Absorption Bands of 3-Hydroxy-3-penten-2-one (in CCl₄)

Absorption bands, cm⁻¹	Assignment
3422 (m)	OH stretching, bonded
3086 (uw), 3066 (vw)	CH stretching on double bond
2974 (w), 2934 (w)	CH₃ asymmetric stretching
2914 (w), 2854 (w)	CH₃ symmetric stretching
1679 (ms)	C=O stretching in α,β-unsaturated
1652 (vs)	C=C stretching
1344 (vs)	CH₃ symmetric stretching in plane and deformation in CH₃C(=O)
1240 (s)	C—C(=O)O asymmetric stretching
1055 (ms)	C—O stretching in C—OH

In order to confirm the existence of the enol in pure form, the buttery caramel aroma compound was stabilized by conversion to its trimethylsilyl (Me₃Si) ether immediately after gc trapping. The enol Me₃Si ether is stable in pure liquid form, or in nonpolar solvents. No free enol or keto form was detected by gc or ir. The ir spectrum is shown in Figure 2. The silylation reagents do not catalyze the enolization. No reaction took place between 2,3-pentanedione and the reagents at moderate temperatures.

The free enol form is not stable and reverts to the keto form at room temperature. It can, however, be held for at least 24 hr in a freezer (0°). The assignment of the absorption bands in the ir spectrum of the enol form is given in Table I. In addition to the enolic bands in Figure 1, there are two strong bands at 1720 and 1715 cm⁻¹. These are
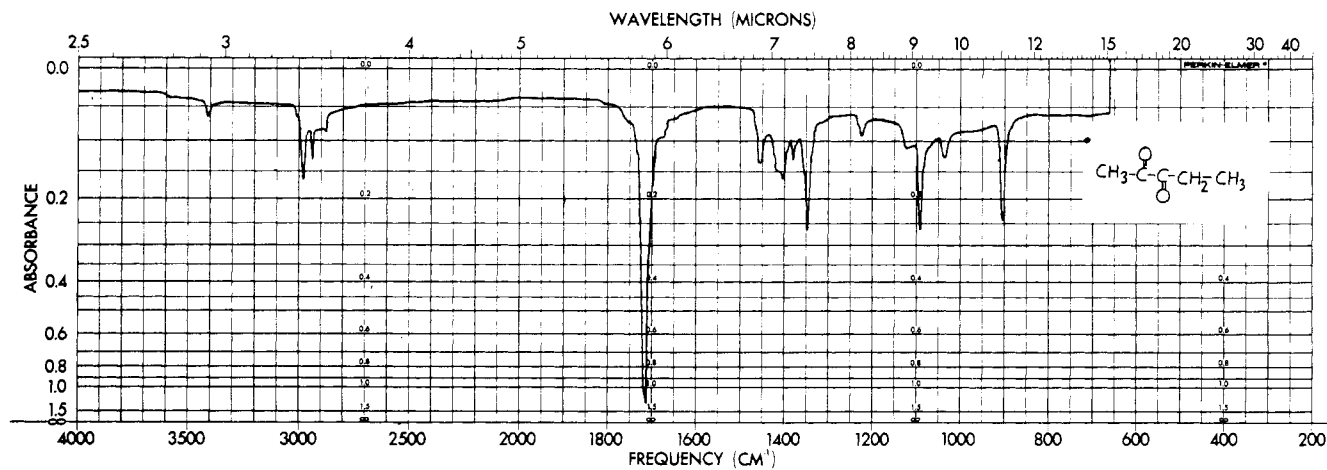
Figure 3. Ir spectrum of 2,3-pentanedione in CCl₄.

Table II. Nmr Spectrum of 3-Hydroxy-3-penten-2-one (60 MHz, CCl₄)

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 Me₃Si 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 Me₃Si 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 Me₃Si 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 Me₃Si 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 cara-

mel 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.

ACKNOWLEDGMENT

LITERATURE CITED

Gerbier, J., C. R. Congr. Soc. Savantes Paris Dep., Sect. Sci. 87, 301 (1962).
Hodge, J. E., "The Chemistry and Physiology of Flavors," Shulz, H. W., Day, E. A., Libbey, L. M., Ed., Avi Publishing Co., Westport, Conn., 1967, p 481.
Koltsov, A. I., Kheifets, G. M., Usp. Khim. 40 (9), 1646 (1971).
Schwarzenback, G., Wittwer, C., Helv. Chim. Acta 30, 656, 659, 663, 669 (1947).

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

Western Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture, Berkeley, California 94710.