The Structure of Solerone [5-Acetyldihydro-2(3H)-furanone], a Substituted γ-Lactone Involved in Wine Aroma

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A compound involved in the aroma of wines has been identified as 4-hydroxy-5-ketohexanoic acid γ-lactone [5-acetyldihydro-2(3H)-furanone] through comparison of infrared and mass spectra of the wine isolates with those of a sample synthesized by oxidation of the C-5 hydroxyl of 4,5-dihydroxy- hexanoic acid γ-lactone. Assigned the trivial name solerone because of its ketonic nature and because it is found in wines matured under flor in soleras, it has a pleasant wine-like odor. Its possible relationship to the 4,5-dihydroxyhexanoic acid γ-lactones of flor sherries is considered.

In an earlier investigation of two samples of Spanish fino sherry and one sample of Californian palomino flor sherry, Webb et al. (1967) did not succeed in completely purifying and identifying the material responsible for gas chromatographic peak 52. The relatively small amount of material available and the fact that the substance giving rise to peak 53 tended to remain with peak 52 as an impurity on both of the gas chromatographic columns being used for purification accounted for the incomplete identification. Impure peak 52 material had a pronounced wine-like aroma and gave an infrared spectrum with a predominant ketone absorption. In general, the concentration in a sherry is apparently a function of the period that the wine has aged under the yeast film—some film exposure being necessary to produce or protect the compound—and longer periods seeming to decrease its concentration. For this reason the compound has been referred to as a "sherry aroma" compound and is named "solerone" in recognition of the fact that it has been found so far only in this wine type when matured under film yeast in soleras. The moderate quantity of the unknown material found in aged flor sherries and its intense and very pleasant aroma have made its unequivocal characterization highly desirable.

EXPERIMENTAL

Isolation and Purification of Wine Peak 52. Isolations of peak 52 material were made from a Californian palomino flor sherry and from a sample of South African solera sherry obtained from the K.W.V. cellars in Paarl. For the Californian sample a Loenco dual-column dual-thermal conductivity detector gas chromatograph Model 70 with 0.25-in. o.d. × 10-ft long stainless steel columns packed with either 10% of Aerograph FFAP on 60-80 mesh Chromosorb W or with 10% of SE-30 silicone on Chromosorb W, and helium as carrier gas at 50 ml/min were used. The South African sample was isolated using a Perkin-Elmer Model 900 gas chromatograph with 0.25-in. o.d. × 3-m stainless steel columns packed with 10% of FFAP or 10% of SE-30 on

60-80 mesh Chromosorb W, AW, HMDS. Flame ionization detection, nitrogen carrier gas at 50 ml/min, and an effluent splitter which sent approximately 95% of the sample to the glass capillary tube collectors and 5% to the flame were used. In both cases injectors were at 200° C, detector and effluent plumbing at 250° C, and the column ovens were programmed from 75 to 250° C in a manner to optimize separation of the desired peak: isothermal at 75° C until isoamyl alcohol had cleared the detector; 2° C/min rise to the appearance of peak 35, isothermal until peak 37 had cleared detector; 2° C/min rise to the appearance of peak 46, isothermal until peak 46 cleared detector; 2° C/min rise to the appearance of peak 46, isothermal until peak 46 cleared detector; 2° C/min rise until peak 52 was collected; 10° C/min rise to 250° C, isothermal at 250° C for 15 min. Peak 52 material was collected first from the FFAP columns, and repurified on the SE-30 columns.

Synthesis of 4-Hydroxy-5-ketohexanoic Acid γ-Lactone. Using the technique of Muller et al. (1969), trans-4-hexenoic acid was converted to racemic 4R:5S and 4S:5R 4,5-dihydroxyhexanoic acid γ-lactone. A sample (9.1 mmol) of 30% H_2O_2 was mixed with 88% formic acid (8.8 mmol) and heated at 75° C for 30 min. The mixture was cooled and added dropwise with stirring to 0.1 g of trans-4-hexenoic acid. The mixture was heated at 40° C for 2 hr, cooled, and stirred at room temperature overnight. The lactone was extracted from the hydroxylation mixture with 10 2-ml portions of diethyl ether, dried over anhydrous $MgSO_4$, and the ether was distilled off through a small Vigreaux column.

The crude hydroxylactone was oxidized according to the technique of Collins et al. (1968). The lactone (0.9 mmol) was mixed with Collins reagent ($CrO_3 \cdot$ pyridine complex in CH_2Cl_2) (5.4 mmol) and stirred for 1 hr at 25° C. At the end of this period, the organic layer was decanted and filtered to remove insoluble chromium salts, washed with 10 ml of water, dried over anhydrous Na_2SO_4, and the product isolated on the Loenco gas chromatograph using the FFAP column programmed at 4° C/min from 75 to 250° C as described above. Repurification was done isothermally at 175° C on the SE-30 column in the Loenco instrument as described above. Synthetic solerone had a retention time on SE-30 of about 13 min.

Measurement of Sample Characteristics. Infrared spectra

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of the Californian sample and of the synthetic material were recorded with a Beckman IR-8 spectrophotometer using thin films on NaCl ultramicro cell windows. The infrared spectrum of the material from the South African sherry was recorded using a Beckman IR-7 instrument also with thin films of sample on the window of a NaCl ultramicro cell.

The mass spectrum of the South African sample was determined with a G.E.C.-A.E.I. MS 902 high-resolution mass spectrometer while the Californian material and the synthetic were run on a C.E.C. Model 21-104 mass spectrometer.

The gas chromatographic retention times of solerone obtained from the various sources (e.g., synthetic, different sherries) agree on FFAP and on SE-30.

RESULTS AND DISCUSSION

Shusherina et al. (1957) reported the synthesis of 4-hydroxy-5-ketohexanoic acid γ-lactone (solerone) by the reaction of aqueous sodium acetate with 4-brom-5-ketohexanoic acid; and Machleidt (1963), upon treating $EtO_2C(CH_2)_2C-(OCCH_3)FCO_2Et$ with sodium hydroxide in aqueous methanol, obtained about 5% of solerone as byproduct, along with the principal product 4-acetyl-4-fluorobutyric acid.

Figure 1 depicts the infrared spectrum of the solerone sample synthesized by oxidation of the C-5 hydroxyl of 4,5-dihydroxyhexanoic acid γ-lactone. This sample was purified by gas chromatography on FFAP and SE-30 columns prior to determination of the spectrum. The infrared spectra of the samples extracted from the two sherries were identical with that of Figure 1 in all critical details.

Each of the spectra contains the very strong absorption at 1775 cm^{-1} which is due to the lactone carbonyl stretching, and at 1170 cm^{-1} which reflects the –C–O–C– lactone stretching. The absorptions at 1715 and 1140 cm^{-1} result from the carbonyl stretching in the group attached to the number 4 carbon of the lactone ring. The absorption at 1412 cm^{-1} can be assigned to asymmetrical bending and the absorption at 1355 cm^{-1} to symmetrical bending in the methyl group. The very weak absorption at 1455 cm^{-1} can be assigned to symmetrical bending (scissoring) of the methylene group adjacent to the carbonyl in the lactone ring.

Although it is apparently not uncommon to fail to resolve the absorption bands deriving from the methyl and methylene groups in the region from 2800 to 3000 cm^{-1} when sodium chloride cells are used, in the present case the finding of only one relatively *weak* band at 2920 cm^{-1} is difficult to explain as the molecule does contain one methyl and two methylene groups. Examination of molecular models suggests that one weak –C–H–O–hydrogen bond could be formed involving one of the methylene protons on C-3 with the carbony oxygen on C-5, and that this bond would so orient the molecule that a second weak hydrogen bond could form involving
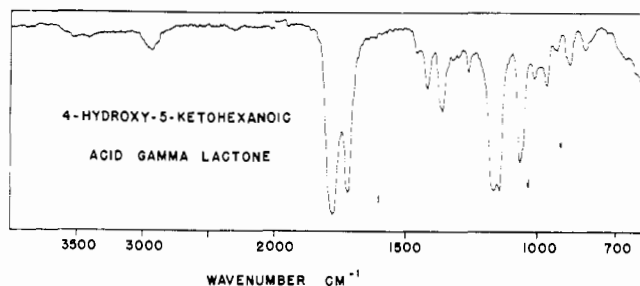

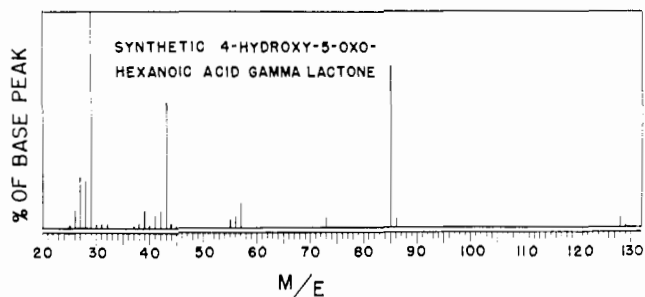Figure 1. Infrared spectrum of synthetic solerone (4-hydroxy-5-ketohexanoic acid γ-lactone)

Figure 2. Mass spectrum of synthetic solerone (4-hydroxy-5-ketohexanoic acid γ-lactone)

one C-6 methyl proton and the ether oxygen of the lactone ring. It seems likely that formation of such hydrogen bonds would reduce the intensity of the methyl and methylene absorptions in the 3000 cm^{-1} region. It is to be remarked that the infrared spectrum of 4,5-dihydroxyhexanoic γ-lactone (Muller et al., 1969), where the C-6 methyl proton to lactone ether oxygen bond also would be possible, shows fairly strong absorptions in the methyl and methylene proton region, thus indicating the greater importance of the carbonyl oxygen to C-3 methylene proton bond in this effect. The weak absorption in the spectrum of solerone at 3500 cm^{-1} may possibly reflect the formation of such intramolecular hydrogen bonds.

In Figure 2 is plotted the mass spectrum of synthetic solerone, 4-hydroxy-5-ketohexanoic acid γ-lactone. The parent peak at m/e 128 is small but recognizable as such. Using the accurate printout of peak heights, calculations show m/e P + 1 equals 8.8% of m/e P (uncorrected for ^{13}C). This is in satisfactory agreement with the value given by Silverstein and Bassler (1967) for $C_6H_8O_3$ of 6.7%.

Silverstein and Bassler (1967) indicate the normal fragmentation pattern for 4-substituted γ-lactones is loss of the substituting group from the number 4 carbon atom. The second largest peak of Figure 2 at m/e 85 certainly arises from this basic γ-lactone ring. The CH$_3$CO– fragment with m/e 43 undoubtedly contributes significantly to the third largest peak. The peaks at m/e 27, 28, and 29 of Figure 2 are, according to Silverstein and Bassler, typical of γ-lactone breakdown and represent the fragments $C_2H_3^+$, $C_2H_4^+$, and $C_2H_5^+$.

The small peak at m/e 41 is probably due to $C_3H_5^+$, and that at m/e 42 is due to $C_3H_6^+$. The peak at m/e 56 is characteristic of γ-lactones and arises from the fragment CH_2—$CH_2C\equiv O^+$. The larger peak at m/e 57 suggests that this C_2H_4CO fragment is able to add a proton with relative ease in the case of the present lactone. The details of the mechanism are unclear but perhaps the postulated weak hydrogen bond involving one proton of the methyl group of the side chain and the ether oxygen of the lactone ring is involved. The spectrum of Figure 2 is completely consistent with the postulated structure of solerone. The fragmentation patterns of the samples of solerone from the sherries agreed with one another and with Figure 2 in all essential details.

When approximately 1 μl of the synthetic 4-hydroxy-5-5-ketohexanoic acid γ-lactone was washed from the sodium chloride infrared cells into an excess of 2,4-dinitrophenylhydrazine reagent in H_2SO_4 and ethanol, a flocculent light orange precipitate was formed. Upon heating in the presence of excess of the dinitrophenylhydrazine reagent, the precipitate dissolved and reformed as a darker reddish-orange colored material. This change in form and color of
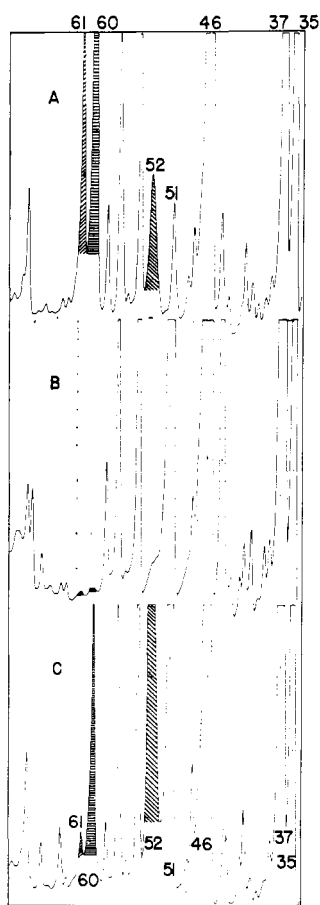
Figure 3. Gas chromatograms of methylene chloride extracts of three sherries showing components emerging after diethyl succinate. A: Spanish flor sherry. B: South African K.W.V. old brown sherry (nonflor). C: South African K.W.V. flor sherry. Peak 35: diethyl succinate. Peak 37: γ-butyrolactone. Peak 46: 2-phenethyl alcohol. Peak 52: 4-hydroxy-5-ketohexanoic acid γ-lactone. Peak 60: 4R:5R and 4S:5S 4,5-dihydroxyhexanoic acid γ-lactone. Peak 61: 4R:5S and 4S:5R 4,5-dihydroxyhexanoic acid γ-lactone

Spanish sherries by Muller *et al.* (1969) raises questions as to whether the two are biosynthetically related, and if so, as to which might normally precede and which follow during the aging of flor sherry wines. To date, the 4,5-dihydroxyhexanoic acid γ-lactones and solerone have been found only in wines which have been grown under the sherry yeast film, and the concentrations of these compounds present in the wine seems to be a function of the length of time the wine has been under the film. Reference to Figure 3, in which are depicted gas chromatograms of three different sherries, shows clearly that the ratio of solerone (peak 52) to the hydroxylactone isomers (peaks 60 and 61) is greater in the K.W.V. solera sample than it is in the Spanish sherry sample. The K.W.V. sample has been aged 2 years under film; the Spanish sample, being a fractionally blended wine containing various proportions of wines of greatly different ages, probably has an average age between 10 and 15 years. The chromatogram of the old brown sherry, a wine which has never been exposed to the film form of the yeast, shows, at most, only trace amounts of the hydroxy- and ketolactones. It is known (Fornachon, 1953) that conditions are highly reducing under an actively growing sherry film. It is thus tempting to speculate that solerone is formed first and later reduced by the action of the sherry film during the period the yeast is actively growing on the surface of the wine in the partially ullaged casks. If, on the other hand, the hydroxylactones were formed first (perhaps as reduction products of yeast during the primary fermentation) and solerone resulted from oxidation during the early stages of aging of the wine, then at least traces of the hydroxylactones should have been found in some of the several young wines which have been carefully checked for their presence. The very close relationship in structure makes it seem likely that the two compounds are biosynthetically related, and the pattern of distribution of the two substances in sherries of different types and ages suggests that solerone is the precursor of the hydroxylactones. The precursors of solerone are unknown at this time.

LITERATURE CITED

Collins, J. C., Hess, W. W., Frank, F. J., *Tetrahedron Lett.* 3363, (1968).
Fornachon, J. C. M., "Studies on the Sherry Flor," Australian Wine Board, Adelaide, Australia, 1953.
Machleidt, H., *Justus Liebigs Ann. Chem.* **667**, 24 (1963).
Muller, C. J., Maggiora, L., Kepner, R. E. Webb, A. D., J. AGR. FOOD CHEM. **17**, 1373 (1969).
Shusherina, N. P., Lur'e, M. Yu., Levina, R. Ya., *Dokl. Akad. Nauk S.S.S.R.* **113**, 1084 (1957); *Chem. Abstr.* **51**, 14669, (1957).
Silverstein, R. M., Bassler, G. C., "Spectrometric Identification of Organic Compounds," 2nd ed., Wiley, New York, N.Y., 1967, pp 24, 40, 91–2.
Webb, A. D., Kepner, R. E., Maggiora, L., *Amer. J. Enol. Viticult.* **18**, 190 (1967).

the derivative can represent simply differences between the syn and anti forms of the derivative, or more likely it can represent hydrolysis or ethanolysis of the lactone, followed by oxidation of the hydroxy group on the number 4 carbon by the excess reagent and precipitation of the 4,5-bishydrazone.

The odor of solerone when freshly purified by gas chromatography is typically wine-like, and has been described as very similar to the odor of the cork from a bottle of old premium quality Pinot noir, or as resembling the odor that lingers in a wine glass several hours after an aged wine has all been drunk from the glass. Pure solerone slowly decomposes on storage in sealed tubes at room temperature, however, yielding a product with little odor. After 3 months' storage the material smelled weakly of fatty acids and gave an infrared spectrum showing alterations principally in the fingerprint region.

The very close relationship of solerone to the 4,5-dihydroxyhexanoic acid γ-lactones found in Californian and