subjecting known mixtures of aldimine isomers to control conditions. In this manner we established that conjugated aldimines would have been detected if 1% had been present after the original reaction. No evidence was found for further reaction between aldimines or pyrrole products and α-amino acids.

The branched chain aldimines obtained from furfural and L-leucine or L-valine were remarkably resistant to isomerization and hydrolysis and they were steam distilled practically quantitatively from aqueous mixtures. In contrast to the results with L-leucine and L-valine, alanine produced ethylamine as the only steam distillable product. Consistent with this observation we found that N-furfurylideneethylamine (prepared from furfural and ethylamine) underwent rapid hydrolysis and decomposition during steam distillation attempts. The apparent intermediacy of a conjugated aldimine in the furfural-alanine reaction suggests that the protonation step (Figure 3) may be quite sensitive to the steric size and electronegativity of the α substituent on the amino acid.

Aroma Properties of Aldimines. Aldimines possessed strong odors ranging from biting and unpleasant to mild and foodlike. In view of the unique aromas of aldimines derived from L-valine and L-leucine several analogs were synthesized for organoleptic evaluation (Table III). Subtle differences in structure such as the position of the imine double bond had marked effects on aroma, e.g., N-furfurylideneisobutylamine produced an unpleasant aroma under conditions where its isomer smelled more chocolate-like.

We concluded that stable aliphatic aldimines may be playing an important role as isoelectronic analogs of aldehydes in browning reaction flavors. The importance of corresponding cyclic aldimines such as 1-pyrroline (Yoshihawa et al., 1965) and 2-acetyltetrahydropyridines (Bucechi and Wuest, 1971) in bread flavor and of trimethyl-3-oxazoline in meat aroma (Chang et al., 1968) has already been well established.

LITERATURE CITED

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Quantitative and Qualitative Analysis of Tangerine Peel Oil
Manuel G. Moshonas and Philip E. Shaw

Seventeen major volatile flavor constituents of cold-pressed tangerine oil were quantitatively and qualitatively analyzed by a gas-liquid chromatograph (glc) with a computing integrator. Quantitative corrections were made for glc detector response factors and high boiling material which would not be eluted from the glc column during the analysis period. The qualitative analysis was extended to include carbonyl constituents, the only group of volatile flavor compounds that had not been systematically investigated in tangerine oil. γ-Elemene is reported as a new citrus component and α- and β-sinensal and thymol methyl ether are reported as new tangerine oil components.

Since cold-pressed citrus oil makes a major contribution to citrus product flavor (Stanley, 1962), knowledge of oil composition is essential to understanding flavor. Individual constituents and their respective quantities are important to desirable flavor and aroma of citrus oils (Nursten and Williams, 1967).

Earlier studies on citrus oils have reported many qualitative analyses (Nursten and Williams, 1967) but relatively few quantitative analyses (Ziegler, 1971). Our laboratory has identified volatile hydrocarbons and alcohols from tangerine, orange, and grapefruit oils (Hunter and Brogden, 1965; Hunter and Moshonas, 1965, 1966). Similarities in these fractions suggested that the carbonyl fraction has the greatest impact on flavor and aroma characterizing each citrus fruit (Moshonas, 1971). Orange and grapefruit carbonyl fractions have been systematically analyzed (Moshonas, 1971; Moshonas and Lund, 1969). Some mandarin (tangerine) oil carbonyls have been reported (Di Giacomo and Calvarano, 1970), but this fraction has not been analyzed systematically. The relatively little quantitative analytical information available on citrus oil components usually involves either groups of compounds (Stanley, 1962) or glc area percent for individual components where glc response factors or percent noneluting (high-boiling) material were not determined (Bernhard, 1960; Kugler and Kovats, 1965; Kita et al., 1969; Ziegler, 1971). Stanley, in 1962, determined quantities of a few individual citrus oil components, and Shaw et al. in 1971, reported weight percent of the 12 main components in Persian lime oil.

The present study reports both qualitative and quantitative analysis of tangerine oil. Qualitative composition of the important flavor fraction, the carbonyls, was determined. Quantitative glc analysis of the 17 major tangerine oil components afforded their weight percentages after glc response factors and percent of high-boiling components

were determined. Three compounds new to tangerine, thymol methyl ether and α- and β-sinensal, and one compound new to citrus, γ-elemene, were identified.

EXPERIMENTAL SECTION

Samples. Tangerine cold-pressed oil was obtained from a Florida plant and stored at 40°F. Authentic samples of individual compounds were either obtained from commercial sources or isolated previously from other citrus essential oils at this Laboratory (Moshonas, 1971; Moshonas and Lund, 1969), with thymol methyl ether being the only exception.

Thymol methyl ether was prepared by treating 150 mg of thymol in 1 ml of tetrahydrofuran with diazomethane in ether prepared with 2.14 g of Diazald (deBoer and Backer, 1954). After 36 hr at room temperature, the reaction mixture was concentrated and the residue separated by glc on an F&M Model 500 instrument equipped with a thermal conductivity detector and a 0.20 in. i.d. × 18 ft column filled with 60-100 mesh Florisil deactivated with 6% water. The fractions were eluted successively with 300 ml of hexane to remove the hydrocarbons (8.5 g), 400 ml of a 50-50 mixture of hexane and ethyl ether to remove the nonalcoholic oxygen-containing compounds (18 g), and 300 ml of ethanol to remove the alcohols (0.5 g). Although most of the carbonyl-containing compounds were in the hexane-ether fraction, all three fractions were analyzed.

Analysis of fractions was carried out on an F&M Model 810 gas chromatograph using the 20% Carbowax 20M column under the conditions discussed above with the fol-
Table II. Carboxyl Compounds Identified in Tangerine Peel Oil

<table>
<thead>
<tr>
<th>Octanal</th>
<th>Perillaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decanal</td>
<td>α-Sinensal*</td>
</tr>
<tr>
<td>Undecanal</td>
<td>β-Sinensal*</td>
</tr>
<tr>
<td>Dodecanal</td>
<td>Carvone</td>
</tr>
<tr>
<td>Neral</td>
<td>Geranyl acetate</td>
</tr>
<tr>
<td>Geranial</td>
<td>Neryl acetate</td>
</tr>
<tr>
<td>Citronellal</td>
<td>Thymol methyl ether*</td>
</tr>
</tbody>
</table>

* Isolated and identified as a component of tangerine peel oil for the first time. † Isolated in the carbonyl fraction.

No meaningful flavor evaluation of citrus oils can be made without accurate quantitative data. This report does not provide the complete answer to tangerine oil flavor but does provide the identity and an accurate determination of the quantity of each major volatile constituent. It also points out two major constituents unique to tangerine, thymol methyl ether and γ-elemene, which might be used to determine tangerine oil purity. Surprisingly, one major constituent, α-sinensal, with an odor threshold in parts per billion (Dougherty, 1971) had not been previously found as a tangerine flavor component. The 14 identified compounds from the systematic qualitative analysis of the carbonyl constituents of tangerine oil are listed in Table II. Particular care was taken to prevent decomposition and/or rearrangement of compounds by using procedures such as vacuum and molecular distillation and water-cooled column for liquid chromatography to keep heat contact to a minimum. Compounds identified include ten aldehydes, two esters, one ketone, and one ether (thymol methyl ether) which was listed because it is the first time this compound has been isolated from tangerine. The carboxyls are particularly important in flavor because each has a potent and distinctive odor. Even the minor ones can influence the full natural flavor and aroma of tangerine oil. The quantitative portion of this study has shown α-sinensal, geranial, citronellal, decanal, and perillaldehyde to be the major carboxyls, thereby showing the remaining carboxyls listed in Table II to be minor but important flavor constituents. The thymol methyl ether also was found in large quantity. Important differences are apparent when these major tangerine carboxyls are compared with the carboxyls estimated to be in major quantity in orange oil (octanal, nonanal, decanal, citronellal, neral, geranial, carvone, α- and β-sinensal, and nootkatone) and grapefruit oil (nootkatone, geranyl acetate, neryl acetate, ocyl acetate, 1,8-p-menthadien-2-yl acetate, citronellyl acetate, 1,8-p-menthadien-9-yl acetate, decanal, and perillaldehyde), indicating that the carboxyls may contribute the largest impact on the characteristic flavor of each fruit (Moshonas, 1971; Moshonas and Lund, 1969). Thus, the major tangerine oil carboxyls contain fewer aldehydes than orange and fewer esters than grapefruit oil.

**LITERATURE CITED**


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Received for review July 16, 1973. Accepted October 29, 1973. Mention of brand names is for identification only and does not imply recommendation by the U.S. Department of Agriculture.