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# Volatile Constituents of Prickly Pear (*Opuntia ficus indica* Mill., *de Castilla* Variety)

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Volatile components of a commercial variety of prickly pear were concentrated by vacuum codistillation with water, followed by ether extraction of the distillate. The concentrate was examined by large bore capillary gas chromatography–mass spectrometry, and 61 compounds were identified. Quantitatively, alcohols are the major class of compound represented, although numerous esters and carbonyl compounds are also present at low concentrations. Some of the more interesting compounds found are a group of saturated and unsaturated nine-carbon alcohols.

*Opuntia* cacti flourish in many hot, semiarid regions of the world, although they are natives of the Americas and were unknown in the Eastern Hemisphere before the beginning of the sixteenth century. In the succeeding years, *Opuntia* species were transplanted to the Mediterranean countries, Africa, and Australia. The rapid growth and abundant quantities of edible fruit produced by certain *Opuntia* species were major reasons for this spread.

Numerous trivial names—prickly pear, Barbary fig, indian fig—have been applied to the fruit. In certain parts of the world, *Opuntia* fruit comprises a significant fraction of the human daily food supply. Mexico has over twelve thousand hectares under commercial cultivation, with an annual production of approximately 120 000 metric tons (Barrera-Benitez, 1976). Eight varieties of prickly pear are grown in commercial quantities in Mexico. The most popular variety, *de Castilla*, is the subject of this study. Commercial production of *Opuntia* fruit in the U.S. is rather small at present; most of the fruit harvested in the country is grown to satisfy the demand for the commodity from the Mexican–American market in the West and Southwest, as well as from Americans of Mediterranean ancestry in the eastern U.S.

The fruit of the *de Castilla* variety is pale yellow-green, rather ellipsoid in shape, approximately 8 cm long and 5 cm in diameter. Most literature references to *O. ficus indica* describe the fruit as red, but the particular commercial variety studied contains no noticeable red pigment. The skin is relatively smooth, with spirally arranged areoles lacking spines distributed across the surface. In cross section, the fruit displays a pale-green interior, similar in texture to that of a ripe melon or Kiwi berry. In contrast to these two examples, however, the small dark seeds or stones are distributed rather uniformly throughout the interior tissue. These are eaten with the pulp, which has a light, somewhat melon-like flavor. It is mildly sweet with little acid character.

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Most of the Mexican crop is sold and used as fresh fruit, with some of this converted by the purchaser into fresh juice. On a smaller scale, a number of concentrated or partly dried products are prepared, including concentrated juices, syrup, preserves and quesos, or semisolid sweets.

All previous research work reported in the literature is confined to nonvolatile constituents of the fruit, including levels of certain nutrients. Total acid (as citric acid) values of 0.084–0.12% were found, with pH ranging from 4.85 to 6.3. The vitamin C level in the fruit was reported to be 42 mg/100 g of fresh fruit (Villareal et al., 1963, 1964; Nordal et al., 1966; Espinosa et al., 1973; Paredes Lopez and Rojos Burgos, 1973). Some work has been reported on the pigments in red and yellow-orange varieties as well (Minale et al., 1965; Impellizzeri and Piattelli, 1972).

## EXPERIMENTAL SECTION

**Starting Material.** *Opuntia ficus indica* Mill., *de Castilla* variety, was grown at San Martin de las Pyramides, Estada de Mexico, Mexico. The fruit was harvested in late September, 1976, and air shipped in corrugated containers to the U.S.

**Concentrate Preparation.** Each end of the ripe fruit was cut off, then the skin was slit longitudinally and peeled back, yielding the intact central portion. The fruit tissue (4.93 kg) including seeds was coarsely chopped and placed in the glass 12-L pot of the stripping apparatus, which has been previously described (Forrey and Flath, 1974). The operation was basically a vacuum codistillation with water, the distillate being collected in a solid carbon dioxide–isopropyl alcohol-cooled receiver flask. Distilled water (3 L) and methyl silicone oil (2 drops; SF (96(50)) were combined in the 12-L pot with the fruit, and the system was evacuated to 40mm. After 3.25 h of distillation, 0.9 L of distillate had collected. The frozen distillate was melted and extracted for 4 h in a conventional liquid–liquid extractor, using freshly distilled ether (125 mL). After being chilled in a freezer, the ether solution was decanted from several drops of water and distilled, using a 30 cm × 1.2 cm glass helix-packed, vacuum-jacketed distillation column, to remove most of the solvent (a water bath was used for heating; maximum temperature = 45 °C). The residue (ca. 2 mL) was transferred to a small vial fitted with an 8 cm long air condenser, and most of the

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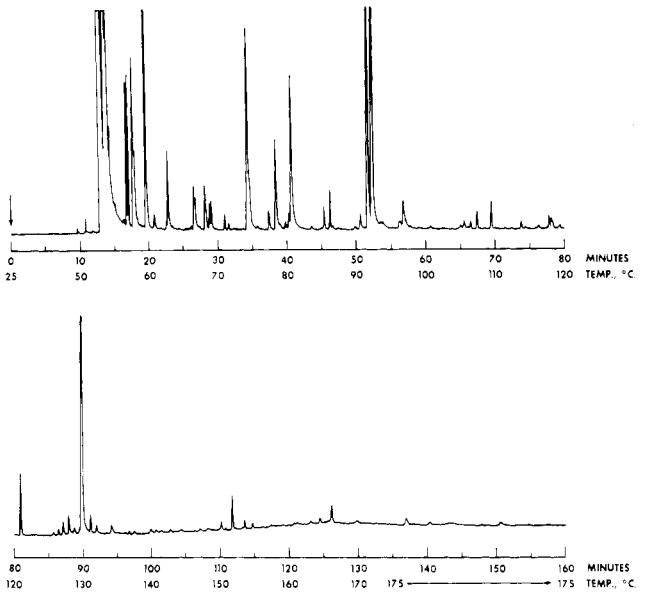


**Figure 1.** Temperature-programmed open-tubular column GC analysis (FID) of prickly pear volatiles; 500 ft × 0.03 in i.d. (152 m × 0.76 mm i.d.) stainless-steel open-tubular column coated with methyl silicone oil SF 96(50) containing 5% Igepal CO 880.

remaining solvent was distilled, again using a water bath (maximum $T$ = 48 °C). Approximately 0.1 g of residue remained in the vial. Gas chromatographic examination revealed this to be approximately 65% solvent, so 35 mg of fruit material was isolated from the starting fruit (yield = 7 ppm).

**Concentrate Separation and Identification.** Gas chromatographic (GC) separations were carried out with a Hewlett Packard 5831A gas chromatograph (flame ionization detector, FID), using large-bore, wall-coated, stainless-steel, open-tubular columns coated with either methyl silicone oil or diethylene glycol succinate polymer.

Component identifications are based upon GC–mass spectrometric data obtained with a quadrupole-type mass spectrometer. Tentative identifications were always substantiated by GC relative retention time determinations for each component. Details of the separation and identification procedure have been reported earlier (Flath and Forrey, 1977).

Area percent values from the GC chromatogram integration are used without correction for FID response variation. For the purposes of this study, uncorrected values are felt to be sufficiently accurate. The largest error is encountered in the quantitation of lower molecular weight compounds such as ethanol and the propanols. The FID is relatively insensitive to such compounds, so the listed values for these components in Table I are somewhat low.

## RESULTS AND DISCUSSION

Identified components are listed in Table I by compound type. The 61 fruit constituents represent ca. 95% of the fruit component chromatogram area. Approximately 140–150 discrete peaks may be seen on examination of the chromatogram, however.

Alcohols comprise by far the major proportion of the concentrate (84 area %), with most of this being due to ethanol. The homologous series of normal primary alcohols from C-1 to C-9 was found, along with other fairly common saturated alcohols. A number of unsaturated alcohols (7.2 area %) are present as well. Many of those listed in Table I are usually found in disrupted plant tissue, especially the hexen-1-ols. Linalool is likewise often identified in fruit

Table I. Volatile Prickly Pear Components

| | |
|---|---|
| **Alcohols** | |
| Ethanol | 13.08[a] (76.33)[b] |
| 2-Propanol | 13.97 (1.55) |
| 1-Propanol | 17.64 (0.81) |
| 2-Methylpropan-1-ol | 22.69 (0.47) |
| 1-Butanol | 26.63 (0.20) |
| 3-Pentanol | 28.93 (0.16) |
| 3-Methylbutan-1-ol | 34.19 (1.40) |
| 1-Pentanol | 38.30 (0.56) |
| Cyclopentanol | 40.17 (0.09) |
| 1-Hexanol | 51.49 (2.20) |
| 1-Heptanol | 64.79 (0.30) |
| 1-Octanol | 77.60 (0.01) |
| 1-Nonanol | 98.70 (0.01) |
| 3-Penten-1-ol | 34.40 (0.24) |
| 3-Methyl-2-buten-1-ol | 40.48 (1.22) |
| *trans*-3-Hexen-1-ol | 49.52 (0.02) |
| *cis*-3-Hexen-1-ol | 50.37 (0.11) |
| *trans*-2-Hexen-1-ol | 52.09 (3.39) |
| Linalool | 80.98 (0.30) |
| *trans*-3-Nonen-1-ol | 87.17 (0.08) |
| 3,6-Nonadien-1-ol (*trans,cis*- ?) | 88.83 (0.04) |
| *trans*-2-Nonen-1-ol | 89.93 (2.13) |
| 2,6-Nonadien-1-ol (*trans,cis*- ?) | 90.20 (0.03) |
| **Aldehydes and ketones** | |
| Acetaldehyde | 11.67 (t)[c] |
| Acetone | 12.00 (t) |
| 3-Pentanone | 26.41 (0.23) |
| 2-Methyl-2-pentenal | 43.39 (0.01) |
| *trans*-2-Hexenal | 46.05 (0.19) |
| Benzaldehyde | 62.49 (t) |
| Acetophenone | 76.07 (0.02) |
| *trans*-2-Nonenal | 86.53 (0.03) |
| β-Ionone | 123.02 (0.01) |
| **Esters** | |
| Ethyl acetate | 19.49 (2.06) |
| Ethyl propionate | 28.66 (0.10) |
| Diethyl carbonate | 36.78 (t) |
| Ethyl butyrate | 39.62 (0.04) |
| Ethyl 2-methylbutyrate | 46.40 (0.02) |
| Ethyl 3-hydroxybutyrate | 60.45 (0.02) |
| Ethyl hexanoate | 66.29 (0.03) |
| Ethyl heptanoate | 79.09 (0.03) |
| Methyl octanoate | 82.43 (t) |
| Diethyl succinate | 88.34 (0.01) |
| Ethyl octanoate | 91.27 (0.10) |
| Ethyl nonanoate | 102.73 (0.01) |
| Methyl decanoate | 104.13 (0.01) |
| Ethyl decanoate | 113.55 (0.05) |
| Ethyl undecanoate | 124.37 (0.03) |
| Ethyl dodecanoate | 136.84 (0.05) |
| Ethyl crotonate | 45.21 (0.11) |
| Ethyl 3-hexenoate | 67.23 (0.09) |
| Ethyl 2,4-hexadienoate | 77.69 (0.09) |
| Ethyl phenylacetate | 96.74 (0.01) |
| Ethyl cinnamate | 121.09 (t) |
| γ-Nonalactone | 110.12 (0.04) |
| γ-Decalactone | 120.61 (t) |
| **Ethers** | |
| (Ethyl ether-solvent) | 13.57 |
| *p*-Dioxane | 28.01 (0.28) |
| 1,1-Diethoxyethane | 31.46 (0.03) |
| **Halides** | |
| (Chloroform-solvent) | 20.67 |
| **Hydrocarbons** | |
| Methylcyclohexane | 30.88 (0.07) |
| Toluene | 35.61 (0.02) |
| Myrcene | 66.29 (0.01) |
| Limonene | 71.21 (t) |
| γ-Terpinene | 73.61 (0.04) |

[a] Retention time in minutes, Figure 1. [b] Area percent of component peak, Figure 1; uncorrected for FID response variation. [c] "T" signifies an area percent of less than 0.01.

volatiles. The nonen-1-ols are somewhat less common, and the relatively large amount of 2-nonen-1-ol (2.1 area %) is of interest. MS data indicate the presence of three nonadienols at 88.83, 90.20, and 92.06 min. The first two of these have mass spectra and GC retention values identical with those of *trans,cis*-3,6-nonadien-1-ol and *trans,cis*-2,6-nonadien-1-ol, respectively. The third could not be further identified.

Carbonyl compounds were identified, but only two, 3-pentanone and 2-hexenal, are at concentrations greater than 0.1%.

Esters as a class are quite common in fruit material, and a rather diverse group has been identified in the present study. Quantitatively they represent less than 3% of the total chromatogram area. Saturated esters comprise most of this total. Relatively few unsaturated or aromatic esters could be detected. The component at 111.79 min (0.1%) is thought to be an ethyl decenoate. Its MS is nearly identical with that of ethyl *trans*-3-decenoate, but its retention time is approximately 2 min too short. A strong 88 fragment suggests that the unknown is not a 2-decenoate. A sample of the *cis*-3-decenoate was not available. Diethyl carbonate is present at trace level.

Very few compounds with ether linkages are present. Dioxane was detected, but is not normally found in plant material. It may be a contaminant, although considerable care is taken in our laboratory to avoid such problems. The small amount of acetal (1,1-diethoxyethane) is most likely an artifact, considering the high concentration of ethanol and the presence of acetaldehyde in the volatiles mixture.

The terpene hydrocarbon content of *O. ficus indica de Castilla* is quite small. Only three could be found, at very low concentrations. Several very minor constituents have mass spectra similar to those of the $\alpha$- and $\beta$-farnesenes, but these could not be further characterized. Small amounts of methylcyclohexane and toluene were also identified.

Diethyl ether was found, but this is because of its use as the extracting solvent. Similarly, traces of chloroform appeared, but this solvent is used to clean syringes in our laboratory.

A degree of uncertainty about double bond geometry in unsaturated compounds always remains when identifications are based upon mass spectral and gas chromatographic data alone. This is evidenced in Table I, where the unsaturated compounds listed do not always have their olefinic configuration specified. In most instances, the cis and trans isomers of, for example, an unsaturated alcohol or aldehyde, can be separated on the open tubular columns employed in this study (cf. *cis*- and *trans*-3-hexen-1-ols). However, for differentiation by retention time, both isomers should be on hand. Similarly, the mass spectra of the cis and trans isomers of volatile unsaturated compounds are frequently sufficiently different that the proper identification of an isomer is possible, if clean spectra of authentic samples of both isomers as well as the unknown are available. In practice, the above conditions of sample availability do not often prevail, and likely geometry is deduced from earlier work with similar materials. For example, 2-enols and 2-enals are usually trans, while the corresponding 3-olefinic compounds are usually present in plant materials as the cis isomers (Flath et al., 1973). On this basis, and because an authentic sample of each trans isomer was on hand for GC and MS comparison, both 2-hexen-1-ol and 2-nonen-1-ol are listed as the trans isomers. The mass spectrum of a component eluted at 88.05 min (0.11%) is nearly identical with that of authentic *trans*-3-nonen-1-ol, the compound eluted at 87.17 min, and is most likely *cis*-3-nonen-1-ol. However, no authentic sample was available, so the cis isomer is not listed in Table I. The double bond configuration of the two nonadien-1-ols are only tentatively indicated in Table I. Only the trans,cis isomer of each was on hand, so other isomers cannot be excluded, although the GC and MS match of each unknown with the respective samples is very good.

Many of the components in Table I have been previously found in a diverse assortment of fruits and cannot be considered unique to prickly pear. However, the presence of 1-nonanol, several nonen-1-ols, the nonadien-1-ols, and 2-nonenal, along with the light melon-like flavor character of the fruit, invite comparison with the published findings of Forss (Forss et al., 1962) and Kemp (Kemp et al., 1971, 1972ab, 1973, 1974ab; Kemp, 1975) on cucumber and melon volatiles. The C-9 compounds found in prickly pear, along with other C-9 mono- and di-unsaturated alcohols and aldehydes were shown to be present in cucumber and certain melons. Melon or cucumber character has been attributed to several of these (Kemp et al., 1974b).

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