Volatile Components of the Orchid *Dendrobium superbum* Rchb. f.

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A gas chromatographic–mass spectrometric study of the porous-polymer trapped volatiles from *Dendrobium superbum* Rchb. f. were examined by GC–MS, because the blossoms are attractive to the male melon fly *Dacus cucurbitae* Coq. Twenty-five components, mostly methyl ketones and 2-alkyl acetates, were identified. 4-Phenylbutan-2-one, structurally related to the known male melon fly attractants 4-(*p*-acetoxyphenyl)butan-2-one ("cue-lure") and 4-(*p*-hydroxyphenyl)butan-2-one, was found, but the two known attractants could not be detected. The major components of the trapped volatiles are ethyl acetate and 2-tridecanone.

The male melon fly (*Dacus cucurbitae* Coq.) is attracted to the blossoms of the orchid *Dendrobium superbum* Rchb. f. We decided to sample the mixture of volatile compounds given off by such blossoms and examine the components by capillary gas chromatography–mass spectrometry (GC–MS). This study was undertaken for two reasons: to identify the volatile constituents of the flower blossoms, in the hope that the attractiveness might be correlated with one or more constituents by subsequent evaluation, and to determine whether the known male melon fly attractants 4-(*p*-acetoxyphenyl)butan-2-one ("cue-lure"; Beroza et al., 1960), anisylactone (Barthel et al., 1957), or the corresponding *p*-hydroxy compound ("raspberry ketone") are present in the volatiles. One of the authors (K.O.) has observed that the scent of the orchid flower is somewhat similar to the aromas of these compounds.

EXPERIMENTAL SECTION

Materials. *Dendrobium superbum* flowers were collected by one of the authors (K.O.) in the Honolulu, HI, area. Tenax-GC (60–80 mesh) was obtained from Applied Science Laboratories, Inc., State College, PA 16801.

Trapping Apparatus. Tenax traps were prepared from 3-in. lengths of 0.250-in. o.d. × 0.226-in i.d. Type 304 seamless stainless steel tubing. The Tenax bed (ca. 120 mg, 1.00 in. long) was retained in the tubing with disks of 325-mesh stainless steel screen, which were in turn supported by coarse (40-mesh) stainless steel screen disks and split retaining rings. During assembly, the Tenax bed was compressed by approximately 15% when the screens were positioned, in order to eliminate any tendency toward channeling in use. Stainless steel Swagelok fittings with stainless steel or Teflon ferrules were used for connecting the traps to other parts of the sampling or desorption apparatus.

Split aluminum blocks fitted with cartridge heaters and an iron–constantan thermocouple were used for heating the Tenax traps during cleaning or desorption of trapped volatiles. A purified helium flow (30 cm^3/min) was passed through the traps whenever they were heated. Traps were baked at 260–280 °C for 16–18 h before use. Clean traps were capped and stored in stoppered glass tubes.

The sampling chamber consisted of a 0.5-gal canning jar fitted with a polycarbonate top plate (Viton o-ring seal), held in place with the threaded metal ring supplied with the canning jar. Two threaded Swagelok fittings were mounted on the polycarbonate plate; a $^1/_4$-in. fitting for attaching the Tenax traps and a drilled-through $^1/_8$-in. fitting. The latter held a $^1/_8$-in. o.d. stainless steel inlet tube that extended down toward the bottom of the sample chamber. The upstream inlet end of this tube was connected with heavy-walled Teflon (TFE) tubing to a glass tube containing granular activated charcoal (10.5 g, 20–30 mesh).

A self-contained battery-operated sampling pump (Model 808 Accuhaler personal sampling pump, MDA Scientific, Inc., Park Rige IL 60068) was used to draw air samples through the Tenax trap. The pump was connected with $^1/_8$-in. o.d. × $^1/_{16}$-in. i.d. Tygon tubing to a 20 cm^3/min (nominal) flow restrictor, which was in turn connected with a Swagelok fitting to the outlet end of the Tenax trap.

Headspace Volatile Collection. The inlet end of a clean Tenax trap was uncapped and immediately connected to the corresponding Swagelok fitting at the outlet of the glass sample chamber. The trap outlet end was then uncapped and connected in turn to the flow restrictor in the sampling pump line. The sampling pump was then started, drawing air through the sample chamber's charcoal-packed inlet filter into the sample chamber. From the sample chamber, air flowed through the Tenax trap and then through the 20 cm^3/min flow restrictor and into the sampling pump. Three collections were made by using separate Tenax traps: a blank run (5 h, approximately 6 L of air sampled); a short sample run (0.5 h, approximately 0.6 L); a long sample run (8 h, approximately 9.6 L). Before the two sample collection runs were made, a 40-g sample of *D. superbum* blossoms was placed in the sample chamber. The same batch of blossoms was used for both sample collections.

In this study, the traps, pump, and sample chamber were sent to the Hawaii laboratory of one of the authors (K.O.). Samples were taken, and the capped Tenax traps were returned to the Berkeley laboratory for examination of collected volatiles.

Trapped Volatile Desorption and Examination. A modification of a previously described (Noble et al., 1980) valving–spiral trap arrangement was used for manipulation of the Tenax-trapped material. The trapped volatiles were back-flushed with a 30 cm^3/min flow of purified helium into a liquid nitrogen cooled spiral trap (12–15-in. length of $^1/_{16}$-in. o.d. × 0.04-in. i.d. stainless steel tubing, wound into a 1-in. o.d. four-turn coil) by heating the Tenax trap for 1.2 h at 155–165 °C.

The volatiles were introduced into the large-bore capillary column by connecting the spiral trap to the column inlet (with appropriate valving), removing the LN bath, and rapidly (10 s) heating the spiral trap to 215 °C with a large heat gun. After an additional 10 s at this temperature, the spiral trap was removed from the carrier

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[1]Deceased.

Table I. Trapped Volatiles from *Dendrobium superbum* Flowers

alcohols		ketones	
ethanol	+[a]	acetone	++
linalool	++	2-pentanone	+++
esters		2-heptanone	+++
methyl acetate	++	2-nonanone	++
ethyl acetate	++++	4-phenylbutan-2-one	++
2-propyl acetate	+	2-undecanone	++
2-heptyl acetate	+	2-tridecanone	++++
2-nonyl acetate	++	2-pentadecanone	++
2-undecyl acetate	+	miscellaneous	
2-tridecyl acetate	+	acetaldehyde	+
hydrocarbons		carbon disulfide	+
toluene	+	indole	++
ethylbenzene	+		
o-xylene	+		
p-xylene	+		
limonene	+		

[a] Crosses indicate the relative amounts of each component in the trapped volatiles mixture.

stream by resetting the valves. The stainless steel capillary column [500 ft × $^1/_{16}$-in. o.d. × 0.03-in. i.d., coated with methyl silicone oil [SF-96(50)] containing 5% Igepal CO-880] was held at 45 °C for 10 min and then was programmed at 1.2–1.3 °C/min to 182 °C, where it was held until completion of the run (40 min). The column exit was interfaced with a quadrupole mass spectrometer (Noble et al., 1980) through a silicone rubber membrane type separator (held at 180–185 °C). Mass spectral identifications were verified by retention index checks, using authentic samples of each component.

RESULTS AND DISCUSSION

Table I lists the compounds identified in this study. Quantitatively, the compounds in this list comprise nearly all of the volatile material trapped.

The largest compound group identified is the odd carbon numbered methyl ketones, ranging from acetone through 2-pentadecanone. The most prominent member of the group is 2-tridecanone; it is one of the two major components of the total trapped flower volatiles.

Ethyl acetate is the other major component of the trapped material and was preceded in the GC–MS run by a trace amount of methyl acetate. The remaining acetates are esters of odd carbon number secondary alcohols, from 2-propyl to 2-tridecyl acetate. A single gap exists in the series, for no 2-pentyl acetate could be detected.

None of the corresponding free secondary alcohols were detected; the only alcohols appearing were ethanol and linalool.

The four aromatic hydrocarbons were all present at very low concentrations. It is unclear whether these were really evolved by the blossoms or whether they are atmospheric contaminants.

Two nitrogen- or sulfur-containing volatiles appeared in the trapped flower volatiles. Carbon disulfide was detected at quite low concentration, and an appreciable amount of indole was also found to be present.

Within the sensitivity limits of the experimental approach, no 4-(*p*-acetoxyphenyl)butan-2-one could be detected, nor was the *p*-hydroxy compound found. The free phenolic 4-(*p*-hydroxyphenyl)butan-2-one survives passage through the GC–MS system, so its apparent absence from the *Dendrobium superbum* volatiles sample is not thought to be due to irreversible adsorption or decomposition during mixture separation. As noted in Table I, 4-phenylbutan-2-one did appear among the sample constituents. The presence of this related compound suggests that the *p*-hydroxy and *p*-acetoxy compounds might yet be present in the flower volatiles but at very low concentrations, too low for detection in the amount of sample trapped for this study.

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Volatile Constituents of Some Central African Black Tea Clones

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The major volatile constituents found in the aroma concentrates prepared from some tea clones of distinct China-type characteristics were similar to those reported for flavory tea produced in India and Sri Lanka. The dominant high-boiling compounds were linalool, *trans*-furanolinalool oxide, and geraniol. Levels of the undesirable low-boiling alcohols and aldehydes, however, were higher in the domestic clonal teas. An important finding was that, contrary to expectation, some of the clones exhibited flavor characteristics during the main production season in this region.

Central African black teas are generally recognized as plain teas, having none of the distinctive flavor associated with the much more valuable product grown at high elevation in certain districts in India and Sri Lanka. The rapid growth during the main production season and the intensive nitrogen fertilizer policy are thought to preclude the development of the flavor precursors, since the biogenesis of the volatile terpenoid compounds is associated with physiological stress in the plant (Wickremasinghe, 1974). During the cool, dry production off-season, in this region, however, flavory teas are sometimes produced, particularly from leaf of China hybrid cultivars.

Previous studies have reported the volatile constituents of teas produced in India (Yamanishi et al., 1968a), Sri

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