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NONANAL IN EPICUTICULAR WAX OF GOLDEN EGG PLUMS (*PRUNUS DOMESTICA*)

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Key Word Index—*Prunus domestica*; Rosaceae; Golden Egg plum fruit; cuticular wax; nonanal; flavour.

Abstract—Nonanal was identified, as a major component, in the aldehyde fraction of the cuticular wax of the plum cultivar, Golden Egg. This compound was found to play an important role in the overall aroma of the plum.

INTRODUCTION

An investigation into the flavour components of plums (*Prunus domestica* L.) showed that one cultivar, Golden Egg, had very little flavour in spite of a strong aroma emanating from the surface. As the skin of this cultivar was covered with a heavy bloom, it seemed possible that the wax layer on this plum was acting as a base in which volatile compounds were being concentrated [1]. Accordingly, an aroma and chemical analysis of the cuticular wax was undertaken.

RESULTS AND DISCUSSION

The cuticular wax layer, removed from whole plums by rapid immersion in CH_2Cl_2, had a creamy, fragrant wood-like odour. These characteristics were considered to make a significant contribution to the aroma of Golden Egg.

PLC of the wax in C_6H_6 yielded seven fractions (Table 1), of which all but the aldehyde fraction were odourless. The qualitative composition of the wax was similar to that reported for prune fruits [2]. However, GLC separation on polar and non-polar columns showed that the 'aldehyde' fraction comprised one major and eight minor components (Table 2). Identifications were based upon MS fragmentation patterns and GLC R_t in comparison with authentic compounds. In addition, nonanal the major component was reduced, with $NaBH_4$, to nonanol, the identity of which was confirmed by its R_t on the two columns. Odour evaluation [3] of the GLC eluate showed that nonanal had the creamy, fragrant woody note, associated with the intact wax fraction. Nonanal has been identified in the volatiles isolated from many fruits and vegetables [4], but it has only been reported to be of significance in the aroma of lemon oil [5], cauliflower and broccoli [6]. It has not been found previously in the fruits of the genus *Prunus*, although it has been isolated from peach leaves [7]. The presence of nonanal, in the headspace of intact plums, and its absence from that of peeled ones, suggests that this aldehyde, being more soluble in non-polar solvents, is preferentially extracted from the aqueous flesh. The identification of relatively low MW volatile compounds trapped by the cuticular wax of the fruit may be a ready means of obtaining information on

Table 1. Composition of epicuticular wax on fruits of Golden Egg plums

Class*	% of wax†	Constituents (% of class)
Alkanes	20.1	C_{21}–C_{31}; C_{27} (4.3), C_{29} (86), C_{31} (2.9)
Alkyl esters	8.2	C_{34}–C_{50}; C_{40} (45.3); C_{42} (20.5), C_{44} (18.5) Esterified primary alcohols: C_{18}–C_{30}; C_{22} (4.9); C_{24} (64.8); C_{26} (16.5); C_{28} (3.9) Esterified fatty acids: C_{12}–C_{32}; C_{16} (15.1); C_{18} (16); C_{20} (10.7); C_{22} (5.1); C_{24} (12.8)
Ketones	1.0	C_{29}-10-one (100)
Aldehydes	1.1	See Table 2
Sec. alcohols	48.3	C_{27}–C_{31}; C_{29}-10-ol (92.7)
Prim. alcohols	3.0	C_{18}–C_{30}; C_{24} (53.3); C_{26} (24.1); C_{28} (9.6)
Fatty acids	0.5	C_{16}–C_{36}; C_{16} (6); C_{24} (14.5): C_{26} (10.8); C_{28} (16.9); C_{30} (14.5); C_{34} (21.7)
Triterpenoid acids	5.4	Oleanolic
	1.0	Ursolic
Unidentified	11.4	Major unidentified compound (5.4% of wax) present in triterpenoid fraction. M^+ (TMSi ether) *m/e* 472, major fragments 229 and 367.

*In order of TLC elution on Si gel G–C_6H_6. †Determined by GLC on a Dexsil 300 column using an internal standard.

Table 2. Volatile compounds isolated from the cuticular wax of Golden Egg plum

Compound*	% Volatiles in wax 'aldehyde' fraction	Odour	MS *m/e* (rel intensity)
o-Xylene†	5	Solvent, pungent	91 (100), 106 (56), 105 (29)
p-Xylene†	5.45		77 (15)
Unidentified	0.9	Creamy	112 (100), 83 (76), 55 (48), 96 (10)
Styrene†	14	Fragrant, faint	104 (100), 103 (40), 78 (29), 51 (28)
Unidentified	0.45	Creamy	85 (100), 102 (56), 114 (43), 118 (24)
Nonanal	49.5	Fragrant, creamy, woody	41 (100), 57 (90), 43 (72), 29 (64), 56 (52), 43 (43), 27 (13)
Hexane-2,5-dione†	5.9	Unpleasant, like insecticides	99 (100), 43 (83), 71 (22), 114 (10)
Benzaldehyde	1.8	Almondy	77 (100), 100 (98), 105 (96), 51 (60), 78 (51)
Naphthalene†	16	Moth balls	128 (100), 51 (30), 129 (25), 63 (18), 102 (14)

*Compounds arranged in the order of their GLC elution on Carbowax 20M. †Possibly due to solvent impurities.

components which contribute to its external aroma. It might provide a means for aroma classification of dessert plums.

EXPERIMENTAL

Extraction and analysis of epicuticular wax and wax volatiles. Intact plums 'Golden Egg' (1 kg) were individually immersed for 30 sec in 1 l. of CH_2Cl_2. The extract was coned to dryness using a rotary evaporator, yielding 280 mg of dried extract. The qualitative and quantitative composition of the CH_2Cl_2 extract was determined using published TLC, PLC and GC–MS methods [9, 10].

Examination of odorous wax fraction. The fraction (R_f in C_6H_6 = aldehyde) was taken up in 1 ml of hexane and examined by GLC and GC–MS.

GLC. Carried out using an FID instrument, with a N_2 flow of 40 ml/min. Injection port and detector temps of 250°. Temp. programming was used from 65–210° at 8°/min, then isothermal. Two columns were used: (i) 3.6 m × 3.2 mm glass column packed with 10% Carbowax 20M. (ii) 3.6 m × 3.2 mm glass column packed with 10% SE30 + 0.5% Carbowax 20M.

MS. Recorded on an LKB 9000 coupled GC–MS operating at 70 eV and a separator temp. of 250°, using same columns as above. He flow was 30 ml/min and the GLC was programmed at 6°/min, otherwise conditions were similar to those for GLC analysis.

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RELATION OF CORTICAL MONOTERPENOID COMPOSITION OF *ABIES* TO TREE AGE AND SIZE

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Key Word Index—*Abies*; Pinaceae; growth rate; monoterpenoids; chemosystematics.

Abstract—Correlations between the monoterpenoid compositions of cortical oleoresin on the one hand and tree age and diameter at breast height on the other, were determined for seven fir species of North America. In most cases neither age nor diameter related significantly to the composition of monoterpenoids, suggesting that it was unnecessary to standardize oleoresin sampling for chemosystematic purposes.

INTRODUCTION

In an earlier paper [1] we reported on changes in composition of cortical monoterpenoids of several species of *Abies* as a function of the age of the cortex, i.e., with the height of individual trees. The data indicated that large changes take place only in the uppermost portions of tree stems, and that the variability within older portions of the stems was minor compared with differences between individual trees. These older portions of the stems included as a rule the areas of bark blistering—the areas where cortical extrusions filled with oleoresin are formed as the result of local enlargement of resin canals. The absence, or near absence, of the mentioned nongenetic changes along the blistered portion of the stem made it possible to use the composition of cortical oleoresins from blisters directly in our chemosystematic studies without any additional corrections.

The terpenoid variability with age of cortex within a plant must be distinguished, however, from the variability with age or size of individual plants. The latter can be studied as a correlation between the percentages of individual terpenoids and age or diameter at breast height (DBH) of trees. In principle, besides nongenetic factors such correlations (i.e. chemophenotypically different compositions of a taxon within different age groups) could also be genetically caused, and could include a dynamic situation with a composition of a gene pool changing in time, or a stationary situation with differences in selection for a particular genotype within specific age groups.