Apricot Glycosidically Bound Volatile Components

Christian Salles,[†,‡] Jean-Claude Jallageas,[†] Françoise Fournier,[§] Jean-Claude Tabet,[§] and Jean C. Crouzet*[,†]

Centre de Génie et Technologie Alimentaires, Institut des Sciences de l'Ingénieur, Université de Montpellier II, 34095 Montpellier Cedex 5, France, and Laboratoire de Chimie Organique Structurale UA CNRS 455, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

Apricot glycosidically bound components separated from the heterosidic pool by silica gel chromatography, gel filtration, and preparative overpressured layer chromatography (OPLC) were studied by negative ion chemical ionization (NICI) and negative ion desorption chemical ionization (NI-DCI) mass spectrometry (MS) and tandem mass spectrometry (MS/MS). The low-energy collisionally activated (CAD) fragmentation patterns and the use of chromatographic retention data (OPLC and HPLC) have allowed the identification of linalyl, α-terpinyl, neryl, geranyl, and benzyl glucosides. The presence of linalyl arabinoglucoside was established by identification of the glucoside derivative obtained by partial enzymatic hydrolysis. The MS and MS/MS spectra agree with the presence of hexyl glucoside and 2-phenylethyl arabinoglucoside. In the presence of ND_3 as reagent in mass spectrometry shifts of 3 mass units were indicative of the presence of linalool oxide glucosides (four isomers detected) and shifts of 4 mass units were characteristic of the four dienediol glucosides isolated. One dienediol arabinoglucoside was also tentatively identified using the same method. These results show that glucosides are the major glycosidically bound volatile compounds present in apricot.

INTRODUCTION

The apricot aroma is dependent on the presence of several volatiles including carbonyl compounds, benzaldehyde, terpenic alcohol, and lactones (Chairote et al., 1981).

Lactones, which have been identified by several authors (Tang and Jennings, 1968; Molina et al., 1974; Chairote et al., 1981; Guichard and Souty, 1988; Takeoka et al., 1990) and are responsible, according to Chairote et al. (1981), for background aroma of the fruit, are more important in some cultivars such as Polonais and Rouge du Roussillon (Guichard and Souty, 1988).

Besides these compounds, terpenic alcohols, linalool, 4-terpineol, α-terpineol, nerol, and geraniol (Tang and Jennings, 1967; Rodriguez et al., 1980; Chairote et al., 1981), develop with 2-phenylethanol the fruity and floral characteristics of the fruit. However, according to Guichard and Souty (1988) only α-terpineol, 4-terpineol, and linalool are detected in extracts obtained from fresh apricot by vacuum distillation and are considered by these authors as contributors for the fruity aroma of several cultivars.

During fruit processing or heat treatment of apricot puree (Crouzet et al., 1984) an enhancement in concentration of furanoid linalool oxides, nerol oxide, and α-terpineol was observed. In these conditions the presence of bound volatiles previously identified in muscat grapes (Williams et al., 1982a) was postulated. The presence of glycosidically bound volatile components in apricot Rouge du Roussillon was confirmed using the rapid analytical technique described by Dimitriadis and Williams (1984). The values obtained for free and bound terpenes as well as for their ratio are of the same order of magnitude as for muscat grapes (Salles et al., 1988). *trans*-Linalool oxides, linalool, α-terpineol, nerol, geraniol, benzyl alcohol, and 2-phenylethanol were isolated after acid and enzymatic hydrolysis of a crude heterosidic extract obtained after adsorption on a C_{18} reversed-phase column (Williams et al., 1982b).

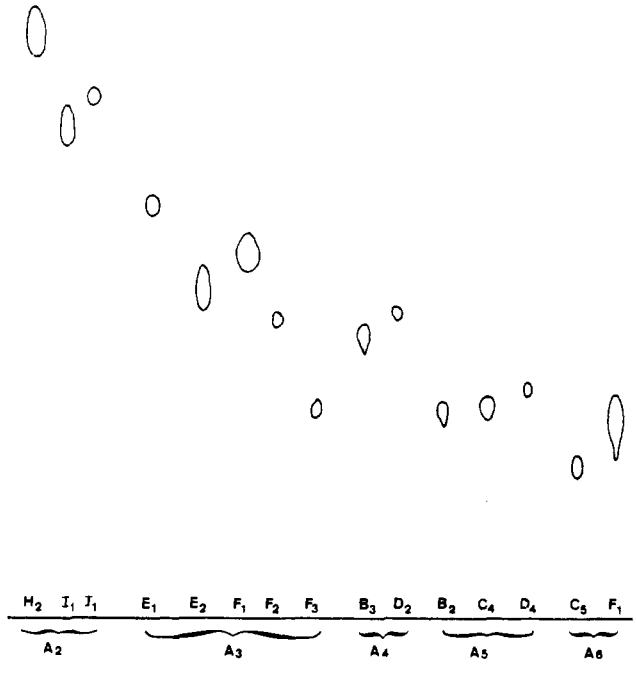

Figure 1. Analytical OPLC of major glycosidically bound fractions separated from apricot (cv. Rouge du Roussillon) heterosidic pool on 0.2-mm silica gel plates (Kieselgel 60, Merck). Eluent: ethyl acetate–*tert*-amyl alcohol–acetic acid–water (18:1:1:1 v/v) at a flow rate of 0.75 mL min^{-1}. Mono- and disaccharidic derivatives were revealed using *N*-(1-naphthyl)ethylenediamine dihydrochloride (Nediac reagent, Merck). The different fractions were numbered as follows: A_2H_2, A as in apricot, 2 is the fraction number in silica gel chromatography, H is the fraction number in Fractogel TSK HW-40 S chromatography, and 2 is the fraction number in preparative OPLC.

Whereas the structure of grape bound volatile components is well established (Williams et al., 1982a, 1983; Voi-

† Université de Montpellier.

‡ Present address: Laboratoire de Recherche sur les arômes, INRA, 17 Rue Sully, 21034 Dijon Cedex, France.

§ Université Pierre et Marie Curie.

0021-8561/91/1439-1979$02.50/0

Table I. Glycosidically Bound Volatile Compounds Identified in Apricot cv. Rouge du Roussillon by Mass Spectrometry (NICI or NI-DCI NH_3 and Low-Energy CAD) and Chromatography

compound	parent ion	m/z and rel abundance of daughter ions 315	179	161	fragmentation mode	retention values: rel migration in OPLC[a]	retention values: retention time in HPLC, min
linalyl glucoside	315		<10	50	2M	1	23.0
α-terpinyl glucoside	315		<10	60	2M	0.89	33.2
neryl glucoside	315		30	10	1M	0.92	39.4
geranyl glucoside	315		25	10	1M	0.89	42.3
benzyl glucoside	269			25	3M	0.68	5.85
linalyl arabinoglucoside	447	100		15	2D	1[b]	23.0[b]

[a] Relative to linalyl glucoside. [b] After partial hydrolysis.

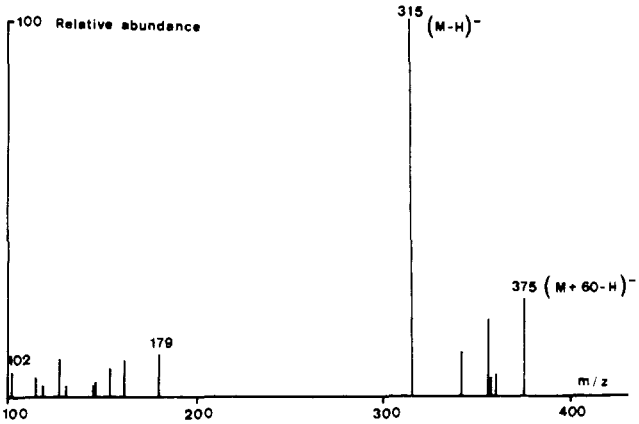

Figure 2. NICI-NH_3 mass spectrum of A_2J_1 apricot fraction (neryl or geranyl glucoside).

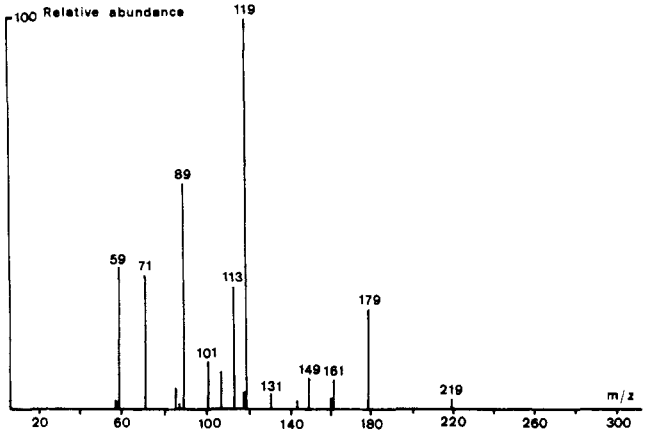

Figure 3. Low-energy CAD spectrum obtained from the molecular species $(M - H)^-$ m/z 315 generated in NICI using NH_3 as reagent gas (Figure 2).

rin et al., 1989), only preliminary studies were devoted to apricot glycosidically bound components (Salles et al., 1988; Krammer et al., 1991).

The aim of the present work was the study of apricot (cultivar Rouge du Roussillon) glycosidically bound compounds separated from the heterosidic pool using chromatographic methods, gel filtration on Fractogel TSK, and OPLC (Salles et al., 1990). In the present study essentially nondestructive methods, soft ionization modes in MS and MS/MS and HPLC, were used. However, in some cases enzymatic hydrolyses were performed for identification purposes.

EXPERIMENTAL PROCEDURES

Plant Material. Mature fruits, cultivar Rouge du Roussillon, were obtained from the experimental orchard of the Institut National de la Recherche Agronomique, Manduel, France.

Apricot halves were crushed at 5–10 °C in a Waring blender and homogenized for 3 min with an Ultraturax at the same temperature; the homogenate obtained was treated for 90 min at 25 °C with 3.0 g L^{-1} Pectinol D5 S (Röhm) and 5.0 g L^{-1} cellulase (Sigma). Clear juices were obtained by two successive centrifugations at 2500*g* for 30 min and 50000*g* for 15 min. It was checked that, in these conditions, added glycosidically bound components, geranyl β-D-glucoside and geranyl β-D-rutinoside, were not or slightly hydrolyzed; less than 10% of rutinoside was converted to glucoside.

Synthesis of Reference Compounds. Geranyl, neryl, α-terpinyl, linalyl, and benzyl glucosides were obtained as indicated in Salles et al. (1990a).

Fractionation of Glycosidically Bound Components. The glycosidically bound components were separated by silica gel chromatography, gel filtration on Fractogel TSK HW-40 S, and overpressured layer chromatography (Salles et al., 1990a).

Thin-Layer Chromatography. TLC was performed as indicated in Salles et al. (1990a).

Overpressured Layer Chromatography. A Chrompres 25 apparatus (Flotec) was used in analytical mode as described in Salles et al. (1990a).

High-Performance Liquid Chromatography. An Analprep 93 pump (Touzart et Matignon) was fitted with a Rheodyne 7125 injection valve, a Lichrosorb RP8 column, 5 μm, 4 × 250 mm (Merck), and a UV 50 detector (Varian) operated at 210 nm. The mobile phase was acetonitrile–water (20:80 v/v) at 1 mL min^{-1}. The compounds separated by HPLC were identified by retention time determination using authentic samples obtained by synthesis or terpenyl glucosides liberated by sequential hydrolysis of glycoside derivatives.

Mass Spectrometry and Mass Spectrometry/Mass Spectrometry. Mass spectrometry experiments were performed on triple quadrupole mass spectrometer NERMAG R-30-10. Negative ion chemical ionization (NICI) and negative ion desorption chemical ionization (NI-DCI) were used respectively for monoglucosides and diglycosides: α-L-arabinofuranosyl β-D-glucopyranosides (arabinoglucosides) and α-L-rhamnopyranosyl β-D-glucopyranosides (rutinosides). The reagent gas, NH_3 or ND_3, was introduced in a modified high-pressure source. The source operating conditions were as follows: emission current, 130 mA; repeller voltage, 0 V; source temperature, 150 °C; ammonia pressure, 9×10^{-5} Torr.

The low-energy collisionally activated decomposition (CAD) spectra of the selected parent ion were obtained using argon at 9×10^{-6} Torr at 10 eV as E_{lab}. The scan rate was 0.5 s for each recorded CAD spectrum using a PDP11/73 computer with a SIDAR system. Each spectrum is the average of 60 consecutive scans from $(M-H)^-$ formed in NICI and about 10 scans from ions produced by DCI probe heating.

Enzymatic Hydrolysis. An *Aspergillus niger* pectinase preparation (Sigma) was partially purified by ultrafiltration (PM 10 Diaflo) and exclusion chromatography on Fractogel TSK HW-55 S. Phosphate–citrate buffer (pH 5, 0.5 mL, 0.1 M), 0.02 mL of partially purified enzymatic preparation (40 nkat using *p*-nitrophenyl α-L-arabinofuranoside as substrate) were added to 0.5 mL of glycoside solution in the presence of 0.05 mL of 0.5 M δ-gluconolactone. It was checked that for this δ-gluconolactone concentration the β-glucosidase activity was totally inhibited when the δ-gluconolactone concentration was between 0.010 and 0.005 M, whereas the glycosidase activities were not affected. The reaction was performed at 25 °C with stirring in a hermetically

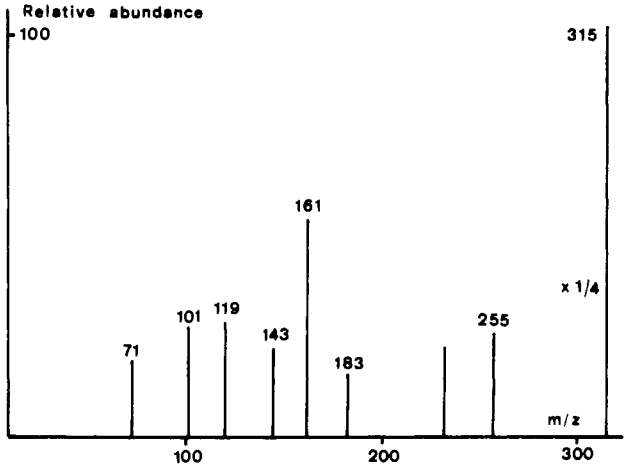

Figure 4. Low-energy CAD spectrum obtained from the molecular species $(M - H)^-$ m/z 447 generated in NICI using NH_3 as reagent gas (linalyl arabinoglucoside).

sealed flask, after 30 min the reaction was stopped by chilling at 0 °C and the reactive medium was analyzed by HPLC.

RESULTS AND DISCUSSION

The major fractions isolated from the heterosidic pool of apricot (Figure 1) were analyzed by NICI or NI-DCI mass spectrometry or tandem mass spectrometery.

Preliminary work carried out using synthetic compounds (Cole et al., 1989a,b) had shown that glycosidically bound terpenic compounds may be distinguished using NICI or NI-DCI MS/MS. In the case of monoglucosides, the relative abundance of the ionic species detected in the low-energy CAD spectra varies according to the nature of the aglycon moiety. More particularly the abundances of fragment ions m/z 179 and 161 were found dependent upon the nature of the aglycon, all other daughter ions, m/z 119, 107, and 89 result from consecutive decompositions of these two ions. From these findings, empiric rules, usable for the tentative identification, were established; three fragmentation modes were defined: 1M (m/z 179 > m/z 161) for geranyl, neryl, and 2-phenylethyl glucosides, 2M (m/z 161 > m/z 119 > m/z 179) for linalyl, α-terpinyl, and citronellyl glucosides, and 3M (m/z 161 abundant and m/z 179 absent) for 1-decyl and benzyl glucosides. An analogous phenomenon was observed for rutinosides, and fragmentation modes 1D (m/z 163 and m/z 205 abundant) for geranyl, neryl, and 2-phenylethyl rutinosides, 2D (m/z 315 very large and more abundant than m/z 161 and 101) for linalyl and α-terpinyl rutinosides, and 3M (m/z 161 > m/z 101) for benzyl rutinoside were defined. It was assumed that these rules were also usable for disaccharidic derivatives other than rutinosides such as arabinoglucosides (Salles et al., 1990b; Fournier et al., 1990).

Monoterpenyl Glycosides. The m/z values for the molecular ion as well as the relative abundance of the daughter ions present in the low-energy spectra of this ion for glycosidically bound components, tentatively identified by Fractogel chromatography and analytical OPLC as terpenic monoglucosides (Salles et al., 1990), are reported in Table I. The application of the fragmentation rules to these fractions has allowed the identification of linalyl, α-terpinyl, neryl, and geranyl glucosides and of linalyl arabinoglucoside (Table I). For example, the presence of the fraction A_2J_1 or A_2K_1 of a deprotonated molecule $(M - H)^-$, m/z 315 in the NICI mass spectrum (Figure 2), and the fact that daughter ions m/z 179 and 161 are present in the low-energy CAD spectra of the molecular ion with

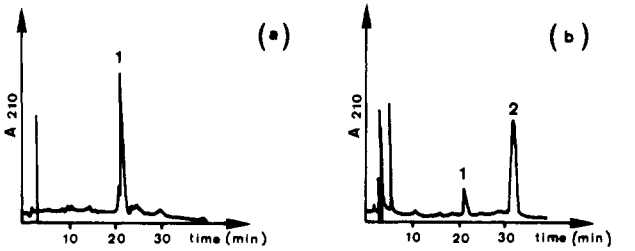

Figure 5. HPLC chromatograms of fraction A_6F_1 (a) before and (b) after partial hydrolysis by *A. niger* pectinase in the presence of δ-gluconolactone. A Lichrosorb RP8 column 5 μm, 4 × 250 mm, was used with mobile phase acetonitrile–water (20:80 v/v) at 1 mL min^{-1}. Detection was at 210 nm. (1) Linalyl arabinoglucoside; (2) linalyl glucoside.

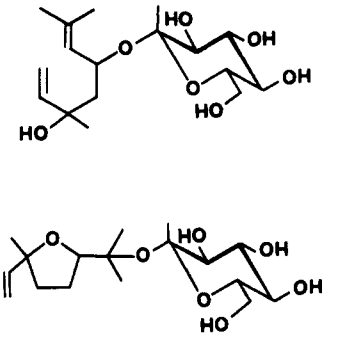

Figure 6.

the relative abundance corresponding to the fragmentation mode 1M (Figure 3) are in agreement with the presence of neryl or geranyl glucoside in this fraction. In the same way the low-energy CAD spectra of the molecular species m/z 315 detected in NICI mass spectra of fractions A_2H_2 or A_2I_1, corresponding to fragmentation mode 2M, are indicative of the presence of linalyl or α-terpinyl glucosides.

The presence of linalyl arabinoglucoside (fraction A_6F_1) was postulated on the basis of the low-energy CAD spectrum obtained from the molecular species at m/z 447 $(M - H)^-$, where fragment ions at m/z 161, 119, and 101 according to the fragmentation mode 2D were detected (Figure 4).

The identity of the different compounds tentatively identified by MS and MS/MS was established by comparison of their relative migration on OPLC and their retention time in HPLC on a reversed-phase column (Bitteur et al., 1989) to those of authentic samples. Linalyl arabinoglucoside was identified by HPLC after action of an *A. niger* pectinase preparation in which α-L-arabinase, α-L-rhamnosidase, and β-D-glucosidase activities were detected. The reaction was performed in the presence of δ-gluconolactone, which is an inhibitor of β-D-glucosidase (Dekker, 1986), to obtain the sequential release of the arabinose unit (Gunata et al., 1988). The decrease of the peak corresponding to the compound initially present and the increase of a peak with the same retention time as linalyl glucoside were observed on the chromatogram (Figure 5). On the other hand, only arabinose and linalyl glucoside were detected by TLC. These results are in good agreement with the presence of linalyl arabinoglucoside in apricot.

Aliphatic and Aromatic Glycosides. In the NICI mass spectrum of the A_3F_2 OPLC fraction, fragment ions and molecular species at m/z 269 $(M - H)^-$, 539 $(2M - H)^-$, and 329 $(M + 60 - H)^-$ corresponding to the adduct given by acetic acid present in the solvent used for OPLC separations are in favor of benzyl alcohol glucoside. The

Table II. Linalyl Oxide Glucosides Tentatively Identified in Apricot cv. Rouge du Roussillon by Mass Spectrometry (NICI NH_3 and ND_3 and Low-Energy CAD)

	parent ion		m/z and rel abundance of daughter ions of $(M - H)^-$		
fraction	NH_3 $(M - H)^-$	ND_3 $(M + 4 - D)^-$	179	161	fragmentation mode
A_3E_1	331	334	<5	55	2M
A_3F_2	331	334	<10	100	2M
A_5D_4	331	334	<10	100	2M
A_4D_2	331	334	<10	100	2M

Table III. Dienediol Glucosides Tentatively Identified in Apricot cv. Rouge du Roussillon by Mass Spectrometry (NICI NH_3 and ND_3 and Low-Energy CAD)

	parent ion		m/z and rel abundance of daughter ions of $(M - H)^-$		
fraction	NH_3 $(M - H)^-$	ND_3 $(M + 5 - D)^-$	179	161	fragmentation mode
A_5B_2	331	335	<10	100	2M
A_5C_4	331	335	60	100	2M
A_6C_5	331	335	12	100	2M
A_4B_3	331	335	100	68	1M

presence in the low-energy CAD spectrum of a fragment ion at m/z 161 and the absence of fragment ion m/z 179 (fragmentation mode 3M) agree with this attribution, which was confirmed by OPLC and HPLC retention data (Table I). Similarly, hexyl glucoside was tentatively identified in the A_3F_1 OPLC fraction, molecular species m/z 263 $(M - H)^-$, 527 $(2M - H)^-$, and 323 $(M + 60 - H)^-$ in the NICI spectrum and m/z 161, fragmentation mode 3M, in the low-energy CAD spectrum.

Phenylethyl arabinoglucoside was tentatively identified in one other OPLC fraction (A_6C_5) as indicated by the NICI spectrum obtained, molecular species m/z 415 $(M - H)^-$ and 475 $(M + 60 - H)^-$.

Dienediol and Linalyl Oxide Glycosides. For several OPLC fractions a parent ion m/z 331 $(M - H)^-$ in the NI-DCI mass spectra may be attributed to a dienediol or a linalool oxide glucoside (MW 332). These compounds cannot be distinguished from their low-energy CAD spectra; however, the differentiation between these two series was made using ND_3 as reagent gas. According to the presence of four acidic protons (Figure 6) in linalool oxide derivatives, the parent ion will be shifted from m/z 331 to 334 $(Md_4 - D)^-$ in the presence of ND_3, whereas with five acidic protons present in dienediol derivatives the parent will be shifted to 335 $(Md_5 - D)^-$ in the same conditions.

A shift of 3 mass units was detected for four components isolated from apricot heterosidic pool when ND_3 was used as reagent gas instead of NH_3 (Table II); all of the low-energy CAD spectra are characteristic of the fragmentation mode 2M. These compounds were tentatively identified as linalool oxide glucosides; this result is in good agreement with previous data (Tang and Jennings, 1967; Rodriguez et al., 1980) relating the presence of the four isomers of linalool oxide among apricot aroma compounds. More recently these compounds were identified after simultaneous enzyme catalysis extraction using emulsin of the apricot glycosidically bound fraction (Krammer et al., 1991).

Four other fractions were tentatively identified as dienediol glucosides according to the 4 mass units from m/z 331 to 335 (Table III).

Finally, a dienediol arabinoglucoside was detected in apricot extract (fraction A_7E_2) according to the presence in its NI-DCI mass spectrum of a parent ion m/z 463 $(M - H)^-$ that was shifted to m/z 469 when ND_3 was the reagent gas used. The presence of four monoterpene diols among aglycons liberated by action of emulsin on apricot glycosidically bound fraction was reported by Krammer et al. (1991).

These findings are in good agreement with preliminary results (Salles et al., 1988) indicating that glucosides are the major glycosidically bound compounds present in apricot, whereas disaccharidic components are predominant in other fruits such as grapes.

The results obtained in the present work show that the use of NICI and NI-DCI MS and MS/MS and more particularly the detection of molecular species and the relative abundance of daughter ions present in the low-energy CAD spectra of these species are valuable tools for the tentative identification of glycosidically bound aroma compounds. More information concerning polyol derivatives may be obtained according to the importance of mass shifts induced by the use of ND_3 in NI-DCI MS. An unambiguous identification of glycosidically bound compounds is obtained when authentic samples are available or when compounds with known structure are obtained through partial hydrolysis of the saccharidic moiety.

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Received for review March 19, 1991. Revised manuscript received July 24, 1991. Accepted August 3, 1991.