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Note

Chiral flavour compounds from apricots

Distribution of γ -lactone enantiomers and stereodifferentiation of dihydroactinidiolide using multi-dimensional gas chromatography

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γ -Lactones possess an intense aroma, often described as fruity, peach or coconut-like^{1,2}. A sensory evaluation of these γ -lactones by a panel, using odour profiling, showed that an apricot note was attributed to the γ -octa- and γ -decalactone³. These evaluations were made on synthetic racemic compounds. Tang and Jennings were the first to identify γ -lactones in apricots^{4,5}. These compounds were later related to the pleasant aroma of the French cultivar Rouge du Roussillon by Rodriguez *et al.*⁶. More recently, Guichard and co-workers^{7,8} found a good correlation between the amounts of γ -octa- and γ -decalactones in six apricot cultivars and the notes attributed by a panel for the typical apricot aroma of these different cultivars. Finally, Mosandl and Günther⁹ demonstrated that the two enantiomers possess different flavour notes in addition to different intensity levels.

The aim of this work was to determine the enantiomeric composition of C₆–C₁₂ γ -lactones in these fruits. The direct stereodifferentiation of C₉–C₁₂ γ -lactones has already been carried out by Mosandl and co-workers^{10–13} by multi-dimensional (MD) gas chromatography (GC)^{14,15} on different commercially available fruit nectars.

EXPERIMENTAL

Apricot samples

Six apricot cultivars, which exhibited different organoleptic characteristics, were analysed. Characterization of the selected cultivars and details of the isolation of the aroma extracts have been described⁷. Apricot slurries were submitted to vacuum distillation under reflux and the distillates extracted with dichloromethane. The amounts of volatile compounds in the concentrated extracts for cultivars harvested in

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1985⁷ and in 1986⁶ have been reported previously. Analysis by GC coupled with mass spectrometry (MS) led to the identification of 82 compounds, 60 of which were found for the first time in this fruit.

Analyses of the extracts

A Siemens Sichromat 2 MD-GC system, with two separate ovens and two flame ionization detectors was used. The carrier gas was hydrogen, with a precolumn pressure $P_A = 0.9$ bar and a main column pressure $P_M = 0.75$ bar. Columns: a fused-silica retention gap (10 m \times 0.25 mm I.D.), according to Grob¹⁶, coupled to a DB-1701 fused-silica column (J & W Scientific) (15 m \times 0.25 mm I.D.), 1- μ m film thickness, coupled to a glass capillary column of heptakis(3-O-acetyl-2,6-di-O-pentyl)- β -cyclodextrin (38 m \times 0.2 mm I.D.). The temperature programme for the precolumn was 90°C isothermal for 2 min, increased at 3°C/min to 200°C, and that for the main column was 90°C isothermal for 20 min, increased at 5°C/min to 170°C.

The chiral main column with modified β -cyclodextrin (Lipodex D) and the modified α -cyclodextrin-containing column (Lipodex B) are now commercially available from Macherey-Nagel (Düren, F.R.G.). Using Lipodex B the 4-alkylated γ -lactones are stereoanalysed in addition to 3,4-dialkylated γ -lactones. For both chiral stationary phases the order of elution of 4-alkylated γ -lactones was proved to be I(*R*), II (*S*) as shown using optically pure references⁹.

Nine extracts were analysed by MD-GC: the six cultivars harvested in 1986, Bergeron harvested in 1985 and Rouge du Rousillon harvested in 1985 and 1988. These last two cultivars possess a typical apricot aroma and contain a large amount of γ -lactones⁸.

To evaluate the relative amount of each enantiomer, peak heights were measured on the gas chromatograms obtained from the heptakis(3-O-acetyl-2,6-di-O-pentyl)- β -cyclodextrin (Lipodex D) column. The proportion of each of the γ -lactones and the proportion of the (4*R*)-enantiomer of each γ -lactone was calculated. As large differences were observed between the amounts of the γ -lactones studied, each extract was injected twice, first with a 1:10 splitting, in order to quantify the highest peaks (hexa-, octa- and decalactone) and then with splitless injection, for the smaller peaks (hepta-, nona- and dodecalactones).

For mass spectrometry (electron-impact mode, 70 eV), a Finnigan-MAT ITD 800 mass spectrometer was used, connected with a DB-5 column (J & W Scientific) (25 m \times 0.32 mm I.D.), 0.25- μ m film thickness.

RESULTS AND DISCUSSION

Fig. 1A shows the chromatographic profile of the C₆-C₁₂ γ -lactones studied on the achiral DB-1701 column. This model solution was injected a second time and cut times were given to transfer each of these lactones onto the Lipodex D chiral column. Fig. 1B illustrates the enantiomeric separation of these synthetic racemic γ -lactones. The (*R*)- and (*S*)-enantiomers are all well separated, thus allowing a good quantification of the enantiomeric composition.

The good repeatability of the retention times on the first column allowed us to transfer, at the same cut times as for the standards, all the γ -lactones contained in the apricot extracts, from the achiral precolumn onto the chiral main column. Fig. 2A

TABLE I
DISTRIBUTION OF γ -LACTONE HOMOLOGUES FROM DIFFERENT APRICOT CULTIVARS

A = Relative amount of each γ -lactone (peak heights were measured on the β -cyclodextrin chromatogram and for each γ -lactone the sum of the two enantiomer peaks was divided by the sum of all the lactones peaks.) R = Relative amount of the (R)-enantiomers [$H_R/(H_R + H_S)$] in percent, where H_R and H_S are the heights of the peak for the (R)- and (S)-enantiomers, respectively].

Cultivar	γ -C ₆		γ -C ₇		γ -C ₈		γ -C ₉		γ -C ₁₀		γ -C ₁₁		γ -C ₁₂	
	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)	A(%)	R(%)
Bergeron 1986	26	88	1	89	13	93	1	83	57	96	tr ^a	—	2	98
Bergeron 1985	21	80	0.8	92	9	92	1.2	89	58	95	tr	—	10	>99
Polonais 1986	18	96	0.6	81	17	92	1.4	76	62	95	tr	—	1	>99
Monique 1986	15	91	0.3	81	10	90	0.7	83	71	95	tr	—	3	99
Palsteyn 1986	49	82	2.5	80	25	90	tr	—	23	92	tr	—	0.5	>99
Precoce de Thyrinthe 1986	87	99	1	81	7	90	0.2	64	4	91	tr	—	0.8	93
Rouge du Roussillon 1988	52	71	0.8	83	20	87	0.6	88	26	97	tr	—	0.6	>99
Rouge du Roussillon 1986	53	71	1.6	90	19	88	0.4	77	22	98	tr	—	4	99
Rouge du Roussillon 1985	29	61 ^b	tr	—	17	86	1	91	42	96	tr	—	11	>99

^a Traces of γ -lactones, not quantified.

^b This low value was confirmed after isolation of this γ -hexalactone from the complex extract by high-performance liquid chromatography [SiO₂, 5 μ m; 1.5 ml/min pentane-diethyl ether (70:30), RI detection]. The eluate in the interval 15–16 min was concentrated and analysed by multi-dimensional GC; *cf.*, separation conditions.

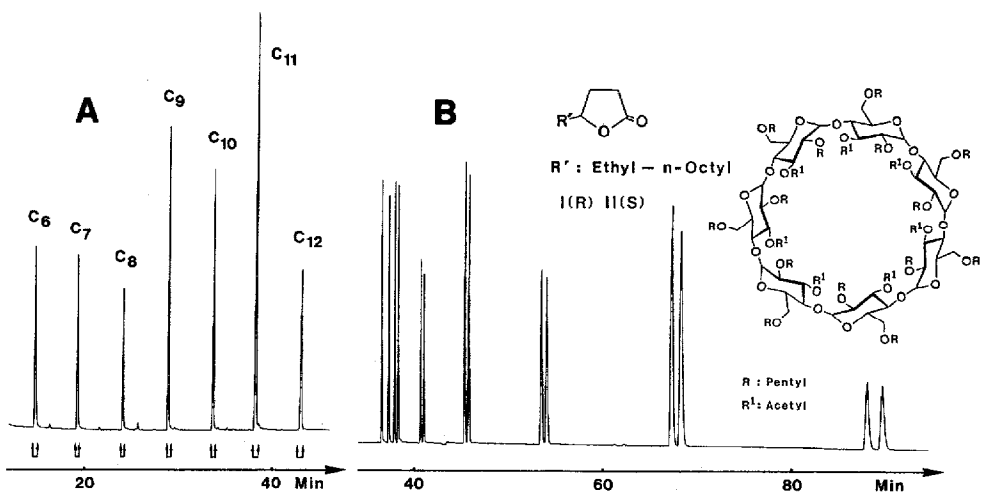


Fig. 1. Multi-dimensional GC of the γ -lactone standard mixture. (A) Preseparation of racemic γ -lactones (C₆-C₁₂) on DB-1701. Conditions: 0.9 bar H₂, column temperature isothermal at 90°C for 2 min, increased at 3°C/min to 200°C. (B) Racemic γ -lactones (C₆-C₁₂) transferred from DB-1701 precolumn onto the chiral main column. Conditions: 0.75 bar H₂ column temperature isothermal at 90°C for 20 min, increased at 5°C/min to 170°C. Order of elution assigned from optically pure references^{9,17}.

illustrates the complexity of one of the extracts and Fig. 2B shows the enantiomeric composition of the transferred γ -lactones. The identity of the peaks was determined by comparison with the GC profile obtained with racemic γ -lactones. Table I gives the proportions of each of the γ -lactones in the extracts investigated and the amounts of the (4*R*)-enantiomers.

Precoce de Thyrinthe and Palsteyn, which are known to be weakly aromatic

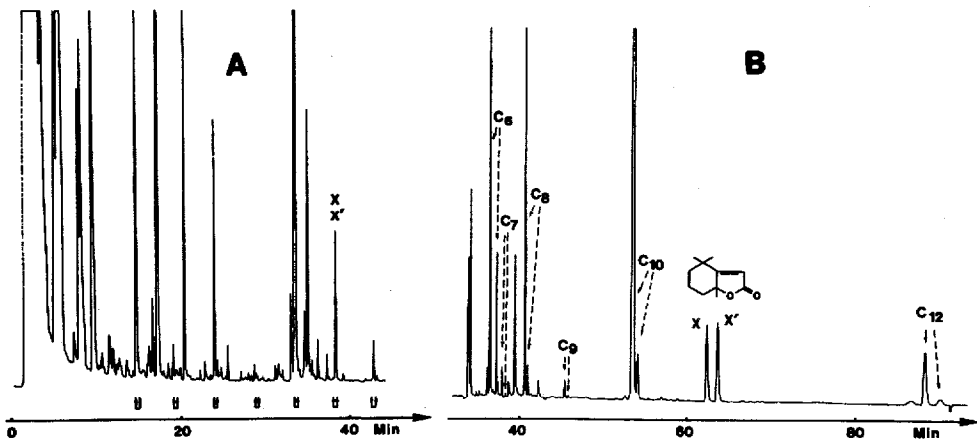


Fig. 2. Multi-dimensional GC of γ -lactones from the apricot cultivar Bergeron (1986). (A) Raw flavour extract, preprepared with with DB-1701. Conditions as in Fig. 1A. (B) Chirality evaluation of γ -lactones with modified β -cyclodextrin as the chiral stationary phase. Conditions as in Fig. 1B.

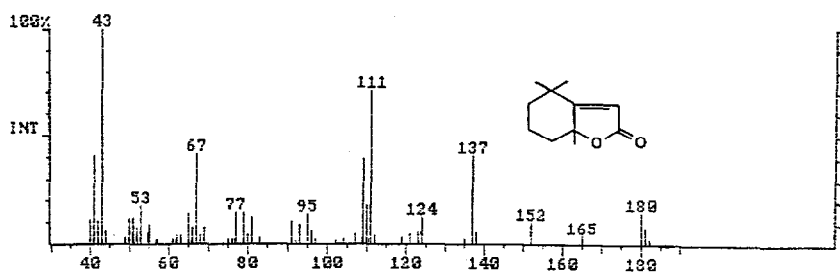


Fig. 3. Mass spectrum (70 eV) of substance XX' from the apricot cultivar Bergeron (1986), identical with the reference dihydroactinidiolide.

cultivars, were poor in lactones, and of these γ -hexalactone was the most abundant. In the other cultivars, which were assessed as more typical⁸, γ -decalactone, with its apricot-like aroma, was present in large amounts and often the most abundant γ -lactone. The γ -octalactone, which would also contribute to the aroma of this fruit, represented between 7 and 25% of the γ -lactones; γ -undecalactone was present only in traces and γ -hepta- and γ -nonalactones did not exceed 2.5%. Only a small amount of γ -dodecalactone was present in all except two of the extracts, in which it reached 11%.

Considering the enantiomeric relationships, it can be seen that the (*4R*)-enantiomer always predominated; γ -hepta-, γ -octa-, γ -deca- and γ -dodecalactone contained more than 80, 86, 91 and 98% of the (*4R*)-enantiomer, respectively. For γ -nonalactone, 64% was found for Precoce de Thyrinthe but the peak was very small and so the precision of the measurement is limited. γ -hexalactone contained a high proportion of the (*4R*)-enantiomer in five out of six cultivars (>80%) and a lower proportion in Rouge du Roussillon (61% in the 1985 harvest and 71% in the 1986 and 1988 harvests). As all extracts were obtained by the same procedure, no explanation could be given for this phenomenon.

As we reported recently⁹, optically pure γ -lactone isomers differ in their odour quality. The (*4R*)-configured γ -hexalactone has a faint and sweet odor. These findings are now confirmed by the sensory judgement of the γ -hexalactone fraction from the investigated apricot flavour extracts. Although high proportions of γ -hexalactone were detected, their contribution to the aroma of the apricots investigated was insignificant. On the other hand, γ -octa- and γ -decalactones in the analysed extracts had a predominantly (*4R*)-configuration (Table I). Their sensory characteristics are known to be spicy-green, coconut and almond notes [(*4R*)- γ -C₈] and strong, fatty-sweet fruity note somewhat reminiscent coconut and caramel [(*4R*)- γ -C₁₀]. This demonstrates that both the relative amounts and the optical purities of chiral flavour compounds are of decisive importance for the aroma profiles of fruits.

A further compound was present as a racemate and was not eluted at a retention time corresponding to a 4-alkylsubstituted γ -lactone (XX', Fig. 2B). This compound was identified as dihydroactinidiolide by coinjection of an authentic reference and the identical mass spectrum (Fig. 3). This compound coeluted with γ -undecalactone on the DB-1701 column and was therefore transferred to the chiral main column. Chairotte *et al.*¹⁸, who identified dihydroactinidiolide for the first time in apri-

cots, suggested that this compound was probably generated during the processing of apricot purée or during the aroma extraction by vacuum steam distillation. However, Guichard and Souty⁷ found this compound in extracts obtained from fresh apricots without any heating. Dihydroactinidiolide is known to be formed by heating of β -carotene¹⁹, but Isoe *et al.*²⁰ obtained it by photooxidation of β -carotene or β -ionone. The formation of this compound by photooxidation can explain the racemic proportions in the extracts of fresh and deep-frozen fruits.

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