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Sorbitol and free sugar contents in plums

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Analytical data are reported for sorbitol and free sugar contents of thirteen cultivars of plums grown in different pedoclimatic areas of Italy. Two chromatographic systems were compared: one using an amino-bonded silica phase (LiChrosorb-NH_2) and the other using a polymeric phase (Polypore Pb). The second phase yielded a sharper resolution of sorbitol from the other sugars with better sensitivity and reliability without the problems of loss of resolution due to ageing of the column. On average, the tested cultivars of plums had a sorbitol content higher than cultivars growing abroad, which are reported in the literature. The variability among the cultivars and the interrelationship between sorbitol and sugars are discussed. The sorbitol content should be included in criteria of plum suitability for drying processing.

INTRODUCTION

Sorbitol is a polyol found in the fruits of 'Rosaceae'. In some species, such as apples and plums, the sorbitol is present in approximately the same concentration as sucrose (Bollard, 1970). This sugar alcohol, together with xylitol, is of growing interest as a substitute for glucose in antidiabetic diets, as well as an alternative natural sweetener to sucrose, so the fruits rich in this compound could be preferred in special diets. Furthermore, sorbitol is effective in drying processes for antibrowning (Stoll, 1970; Labuza & Warren, 1977) and as a humectant (Zimmermann, 1989).

Wrolstad and Shallenberger (1981) established, by statistical processing of the literature data, the characteristic patterns of the individual fruit species relating to their sorbitol content, sucrose content and glucose/fructose ratios. Among the reported species of fruit, pears had the highest content of sorbitol, ranging from 1·2 to 2·8%, on a fresh weight (fr.wt) basis, in the whole fruit and reaching 12% (fr.wt) in concentrated juice. Plums had a lower sorbitol content than pears — from 0·6 to 2·01% (fr.wt) but prunes ranged from 9·4 to 18·8% (fr.wt), and are therefore a good source of this sugar alcohol.

Hartmann (1984) reported the analytical data obtained from over 36 types of plum and damson grown in several locations of Baden Wurttemberg, Germany, in the period 1976–1984. He classified the fruit according to their sorbitol content (on a dry matter basis) and he noticed that the higher the sucrose content the lower was that of the sorbitol. He also observed that the sorbitol content increased with ripening and that it had begun to accumulate only when a certain sugar content was reached.

The same behaviour was reported by Pangelova-Shchrkova and Vitanova (1987). Using an enzymatic method to determine the sorbitol, Weiss and Samaun (1979) found 1·8–13·5% of sorbitol in plum juices.

Data for sorbitol content in plums grown in Italy were not found in the literature. Galoppini *et al.* (1987) reported data of 20 varieties of Italian plums, but only for fructose and glucose. They found from 8 to 13·72% of glucose and from 3·31 to 7·74% of fructose with a glucose/fructose ratio of 1·02–3·87 and a water content ranging from 73·73 to 93·24%. For dried plums they reported 14·37–26·65% of fructose and 44·92–48·27% of glucose with a water content ranging from 24·87 to 35·02%.

The analysis of sorbitol and free sugars in fruit and fruit products can be performed by chromatographic methods. As reported by Wrolstad and Shallenberger (1981), initially the determination of sorbitol together with glucose, fructose and glucose in fruit were performed by TLC (Washutll *et al.*, 1973) or by GLC. Using HPLC analysis, Conrad and Palmer (1976) did not succeed in separating sugars from the correspondent polyols on an amino-bonded silica stationary phase, while they did do so on a polymeric phase. Woidich *et al.* (1978) separated xylitol, fructose, sorbitol and glucose in this order on an amino-bonded phase, but the complete resolution of sorbitol from glucose was obtained only when a strong anion-exchange phase was used. This method was applied to breakfast drinks and chocolates.

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Two different methods for HPLC analysis of sorbitol in fruit were carried out by Brandao *et al.* (1980). One method utilized an amino-bonded phase, while the other method, which used a dual-column system (amino/cyano-bonded phase (PAC) connected in tandem with an amino-bonded phase), allowed a good separation of fructose, glucose, sorbitol, sucrose and lactose within a short time. This latter method was used to analyze sorbitol and maltose in fruit of the 'Rosaceae' family and gave a high content of the polyol in prune plum and a lack in red plum (Richmond *et al.*, 1981)

For the analysis of apple juice and cider, Blanco Gomius *et al.* (1988) compared the performance of the amino-bonded phase with two polymeric strong cation-exchange phases. They found the amino-bonded phase inadequate for the separation of glucose and sorbitol, while the cation-exchange resin in the Ca^{2+} form resolved glucose, fructose, sucrose, sorbitol, glycerol and ethanol very well. The cation-exchange resin in the Ca^{2+} form was used by Mattick and Moyer (1983) and Lee and Wrolstad (1988) for the analysis of apple juice.

Recently Armstrong and Jin (1989) evaluated the efficiency of cyclodextrin-bonded phases. These seemed to be more efficient, stable and selective than amino-bonded silica or ion-exchange resins. However, for the separation of glucose from sorbitol a gradient elution was necessary.

To choose the most suitable method for the analysis of sorbitol in plums, a previous comparison was made between an amino-bonded phase and a cation-exchange polymeric resin the Pb^{2+} form.

This paper deals with the selection of the analytical methods and the results of the analysis of sugars and sorbitol in a group of plum cultivars grown in Italy.

MATERIALS AND METHODS

Fruits

The analyses were conducted on 15 cultivars of plum fruits grown in different pedoclimatic areas of Italy: Bologna (BO), Cagliari (CA), Forlì (FO), Roma (RO). Plums Sel D8 and Tardicotes were divided into dark- and light-coloured fruits by visual sorting. Plums D'ENTE 707 (CA) were analysed for two years (1989 and 1990).

Dry matter and total titratable acidity

Plums were analysed for dry matter and total acidity according to the AOAC (1980) methods. The results are the means of four samples.

Sugar analysis

Ten grams of plums were homogenized with 30 ml of water and centrifuged; the extract was then filtered and the residue was blended with an additional 30 ml of water and centrifuged. The two extracts were brought to volume in 100 ml volumetric flasks. No ethanol was used because it interferes with the sugar peaks in the case of the Polypore PB system. Before the injection into the HPLC the samples were filtered through a Millipore Millex SLHA, 0·45 μm filter unit.

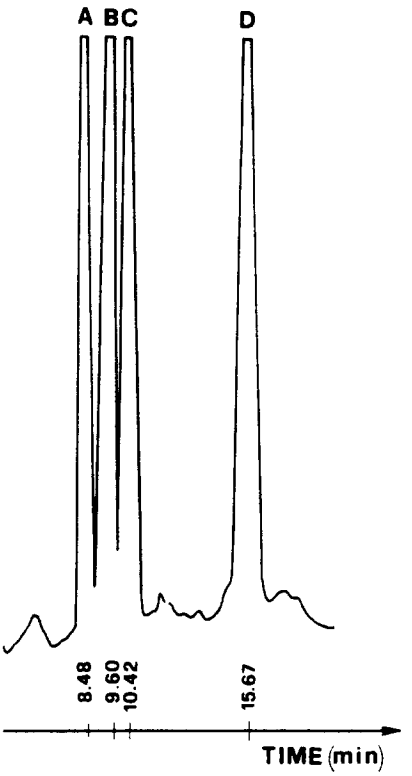

Fig. 1. Chromatogram of a 1% sugar and sugar alcohol standard solution. Column: 25 cm × 4 mm LiChrosorb-NH_2; mobile phase acetonitrile/water (75:25 v/v); flow rate, 1·2 ml/min; detection: IR, att.×4; volume injected, 20 μl. Peaks: A = fructose, B = sorbitol, C = glucose, D = sucrose.

HPLC analysis of extracts

The high performance liquid chromatography used was a Jasco BIP-I (Jasco, Tokyo, Japan). The detector was a Shodex SE11 differential refractometer (Showa Denko KK, Tokyo, Japan). A Shimadzu (Tokyo, Japan) C-R2A Chromatopack data processor was coupled to the detector.

Carbohydrate separations were carried out with two chromatographic systems:

(1) by using a LiChrosorb-NH_2 column (4 mm i.d. × 250 mm) from E. Merck (Darmstad, Germany) with a mobile phase consisting of a mixture of acetonitrile/water (75:25 v/v), previously filtered and degassed under vacuum; flow rate was 1·0 ml/min.

(2) by using a Polypore Pb column (4·6 mm i.d. × 250 mm) from Brownlee Labs (Santa Clara, California, USA), thermostated at 85°C and eluted with water as mobile phase, previously filtered and degassed under vacuum; flow rate was 0·3 ml/min.

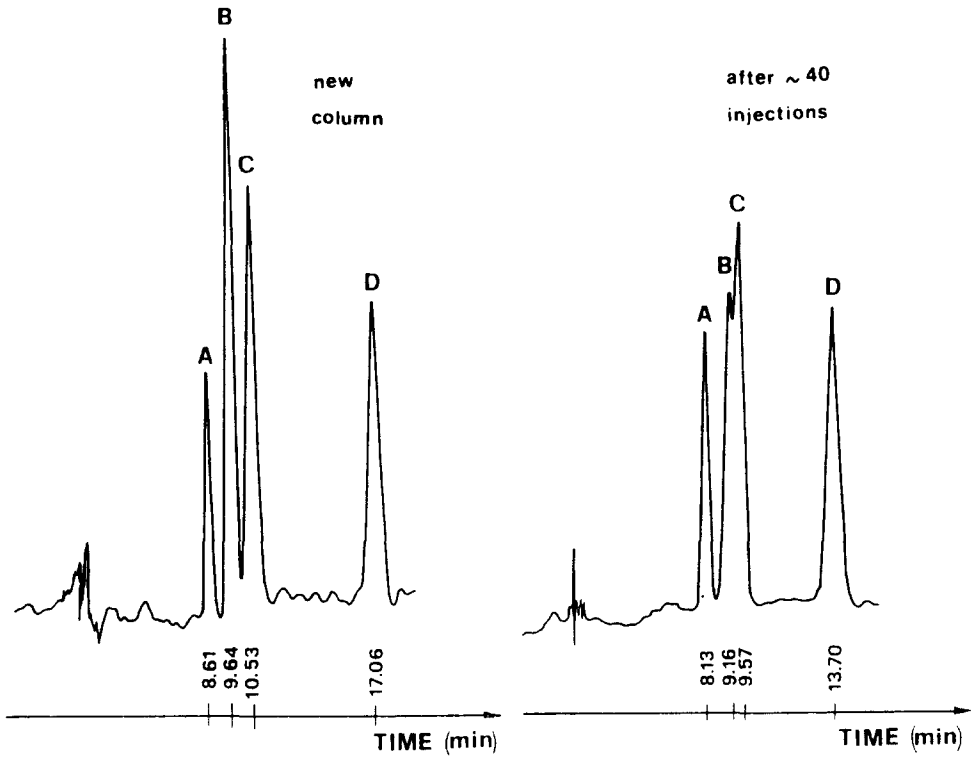

Fig. 2. Chromatogram of plum extract on LiChrosorb-NH_2 column at the beginning of its life and after about 40 injections. Chromatographic conditions and peaks as in Fig. 1.

The solutions of standard sugars prepared were 1% of fructose, glucose, sucrose and sorbitol for the first chromatographic system and 0·1% for the second system because of the different sensitivities of the systems. The concentration of sugars in the samples was obtained by comparing the peak areas of samples to those of the standard solution. The sample volume injected was 20μl. The results were the mean of four replications and were expressed as g/100 g fr.wt. Statistical calculations included the range, mean, standard deviation and percentage coefficient of variance between the cultivars and the geographic origin, and regression analysis between sorbitol and sugars (Larmond, 1977).

RESULTS AND DISCUSSION

Analysis on the amino-bonded silica phase

Figure 1 shows the separation of a 1% fructose, glucose, sorbitol and sucrose standard solution obtained by using a column packed with LiChrosorb-NH_2. The sharp resolution of glucose from sorbitol can be seen. The elution order agrees with that obtained by Woidich *et al.* (1978) with the same column. On the other hand, Brandao *et al.* (1980), using a Microbondapack-carbohydrate column, reported the peak of glucose before that of sorbitol. The relative positions of the peaks of glucose and sorbitol in our chromatogram were ascertained by removing the glucose from the standard solution by oxidation with glucose oxidase (Boehringer, Mannheim, Germany). The quick ageing of this phase is another drawback that leads to the loss of resolution between sorbitol and glucose with a consequent overestimation of glucose, as shown in Fig. 2.

Analysis on a polymeric column

The chromatogram of a 0·1% sugar standard solution separated on a Polypore Pb polymeric column is reported in Fig. 3. The resolution of sucrose, glucose, fructose and sorbitol in this order was very good. The sensitivity was higher than that obtained with LiChrosorb-NH_2; the concentration of the sugars in the standard solution was 0·1% for the polymeric column instead of 1% for the amino-bonded phase, as reported in Figs. 3 and 1, respectively. The lower refractive index of the water used as mobile phase with the polymeric phase compared with that of acetonitrile/water used with the amino-bonded phase could account for this high sensitivity. Our standard sugar analysis agrees with the analyses of Blanco Gomis *et al.* (1988). Figure 4 shows a chromatogram of plum extract on a Polypore Pb column.

The Polypore Pb system was more suitable than the amino-bonded silica phases for the analysis of sugars and sorbitol because of its good column stability and sensitivity, despite some drawbacks such as the higher price and the use of a thermostatic oven.

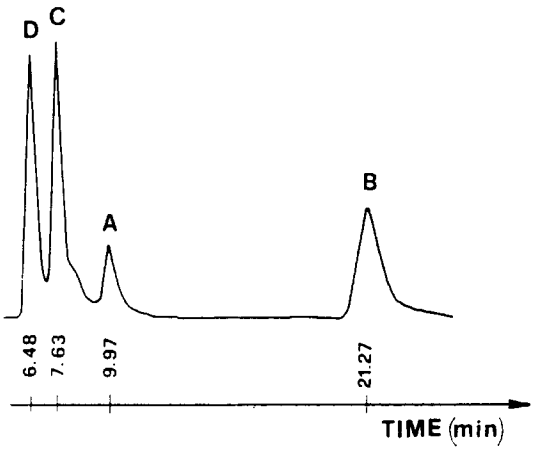

Fig. 3. Chromatogram of a 0·1% sugar and sugar alcohol standard solution. Column: 4·6 mm i.d. × 250 cm Polypore Pb, 10 μm, thermostatted at 85°C; mobile phase, water; flow rate, 0·3 ml/min; detection; IR, att.×4; volume injected 20μl.

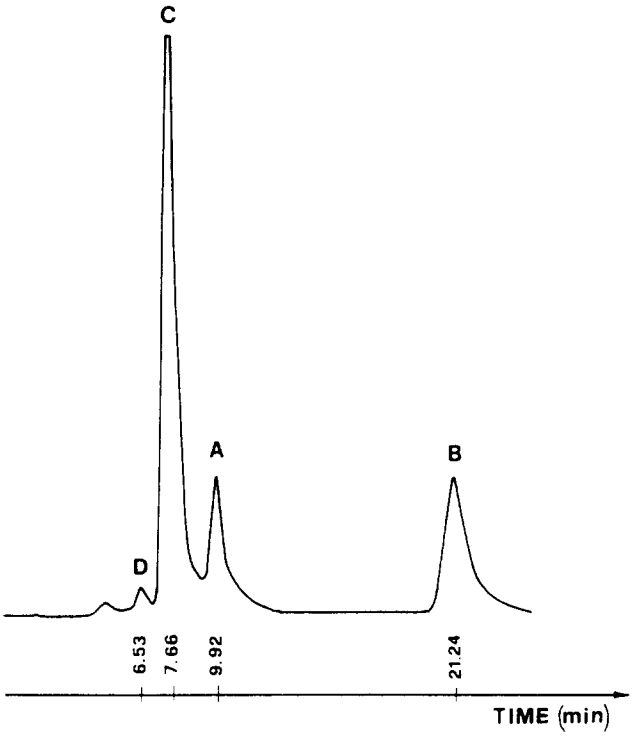

Fig. 4. Chromatogram of a plum extract on a Polypore Pb column. Chromatographic conditions as in Fig. 3.

Analysis of plum fruits

Table 1 reports the results of dry matter and total titratable acidity analyses together with the sugar/acid ratio and glucose/fructose ratio (G/F).

Dry matter showed a mean of 20·86 % with a low per cent coefficient of variance (% CV) with respect to the other parameters examined. Shchrkova and Vitanova (1977) reported a range of 15·93–20·03 for 10 varieties of plums studied in 1975/76.

The values of total acidity ranged between 0·49 and 1·50 g/100 g (fr.wt). Wills *et al.* (1983) reported a range of 0·9–1·9% for many cultivars grown in Australia. Dobreanu *et al.* (1988) obtained values between 0·37% and

Table 1. Analytical data of plums

Plums	Dry matter (%)	Acidity[a] (%)	Sugar acid	Glucose/Fructose
Blue Bel plum (FO)	17·8	0·73	12·7	1·7
BlueFre (RO)	16·6	0·87	11·2	1·5
D'ENTE (BO)	21·5	0·62	15·1	1·8
D'ENTE 707 (CA) 1989	22·0	0·65	13·8	1·8
D'ENTE 707 (CA) 1990	20·6	0·56	12·9	1·4
Prugna D'Argento (FO)	25·0	0·56	22·3	1·3
Stanley (FO)	20·5	0·57	20·6	1·4
Stanley (RO)	20·8	0·64	18·5	1·6
Sugar (BO)	18·2	0·67	11·9	2·1
Sugar (CA)	18·5	0·81	10·3	3·9
Sugar (FO)	19·6	0·71	13·3	2·2
Tardicotes (BO) dark	24·5	0·51	25·6	1·0
Tardicotes (BO) light	24·1	0·49	25·6	0·9
Tuleu Dulce (RO)	23·4	0·77	15·8	1·6
Valor (FO)	19·0	1·50	5·2	1·4
Zucchella (CA)	19·3	0·83	12·1	4·7
Sel B 30 (BO)	20·6	0·82	11·5	1·9
Sel D5 (BO)	22·5	1·14	10·5	5·8
Sel D8 (BO) dark	22·7	1·16	12·7	2·5
Sel D8 (BO) light	20·0	1·15	10·0	2·9
Range	16·6–25·0	0·49–1·5	5·2–25·6	0·9–5·8
Mean	20·86	0·79	14·98	2·17
SD	2·33	0·26	5·54	1·26
% CV	11·17	33·45	36·97	58·29

Table 2. Sugars and sugar-alcohol contents of plums

Plums	Sorbitol (% fr.wt)	Sucrose (% fr.wt)	Glucose (% fr.wt)	Fructose (% fr.wt)	Total sugars (% fr.wt)	Sorbitol (% dry wt)	Sorbitol (% total sugars & Sorbitol)
Blue Bel plum (FO)	1·76	3·49	3·69	2·17	9·35	9·89	15·8
BlueFre (RO)	1·00	3·06	4·05	2·60	9·71	6·02	9·3
D'ENTE (BO)	2·28	3·05	4·02	2·22	9·29	10·6	19·7
D'ENTE 707 (CA) 1989	2·67	2·15	4·45	2·39	8·89	12·1	22·9
D'ENTE 707 (CA) 1990	2·89	3·79	5·03	3·59	12·4	14·0	18·9
Prugna D'Argento (FO)	2·37	4·08	4·72	3·62	12·4	9·48	16·0
Stanley (FO)	2·38	4·69	4·17	3·02	11·9	11·6	16·7
Stanley (RO)	2·56	3·97	4·88	2·99	11·8	12·3	17·8
Sugar (BO)	1·89	5·06	2·02	0·96	8·04	10·4	19·0
Sugar (CA)	2·47	2·39	4·74	1·20	10·1	13·4	22·9
Sugar (FO)	1·81	4·69	3·84	0·94	9·47	9·23	16·0
Tardicotes (BO) dark	2·77	2·05	5·46	5·23	12·7	11·3	17·9
Tardicotes (BO) light	3·13	1·96	5·11	5·45	12·5	13·0	20·0
Tuleu Dulce (RO)	3·98	4·46	4·75	2·95	12·2	17·0	24·7
Valor (FO)	1·67	2·03	3·43	2·38	7·84	8·78	17·6
Zucchella (CA)	2·30	5·46	3·68	0·78	9·92	11·9	18·8
Sel B 30 (BO)	2·94	4·05	3·58	1·87	9·50	14·3	23·6
Sel D5 (BO)	3·12	5·92	4·93	0·76	11·6	13·9	21·2
Sel D8 (BO) dark	5·33	6·27	6·02	2·41	14·7	23·5	26·6
Sel D8 (BO) light	2·92	5·03	4·78	1·78	11·6	14·6	20·1
Range	1·00–5·33	1·96–6·27	2·02–6·02	0·70–5·45	8·04–14·7	6·02–23·4	9·3–26·6
Mean	2·61	3·88	4·37	2·46	10·8	12·4	19·3
SD	0·91	1·34	0·86	1·32	1·82	3·60	3·83
% CV	34·9	34·5	20·0	53·4	16·8	29·1	19·9

0·58% on four species of Romanian plums. Shchrkova and Vitanova (1977) reported a range of 0·70–1·27, while Galoppini *et al.* (1987), analysing 24 cultivars grown in Italy, obtained a range of 0·59–1·47% in agreement with our results.

The sugar/acid ratio, a common index for ripening and quality, ranged from 5·2 to 25·6. Galoppini *et al.* (1987) reported a mean value near 8, but they considered only glucose and fructose and not sucrose for the calculations while Dobreanu *et al.* (1988) reported a range between 25 and 42 and Shchrkova and Vitanova (1977) a range between 8·52 and 15·00. In a work on the quality criteria of fruits, Vangdal (1985) reported that, for good quality plums, this ratio should be between 12 and 24.

The glucose/fructose ratio ranged from 0·9 to 5·8, with a % CV greater than that of the % CV for glucose or fructose content, because the variability for both of these sugars is increased in the calculation of the ratio. Our results agreed with those of the compilation of Wrolstad and Shallenberger (1981). They ordered (in groups) the examined fruits according to their G/F: pear and apple contain much more fructose than glucose (G/F between 0·12 and 0·65), raspberry, blackberry, grape, strawberry and cherry with a G/F near 1 and plum and peach with more glucose than fructose (G/F between 0·88 and 3·44 for plum and between 0·63 and 4·62 for peach). We also calculated the G/F from the glucose and fructose data reported by Galoppini *et al.* (1987); the results obtained ranged from 1 to 3·87.

Table 2 shows the sorbitol and the free sugar contents of plums. The total amount of the free sugars examined ranged from 8% in Sugar (BO) to 14·7% in Sel D8 (BO) dark with a low % CV of 16·8. Dako *et al.* (1970) reported, for 12 samples of plum fruits analysed over a period of two years, a range for total sugar content from 6·33 to 10·83% and Shchrkova and Vitanova obtained a range between 8·60 and 13·50%. Wrolstad and Shallenberger's (1981) data ranged from 5·25 to 13·2% but with a high % CV of 26·3, while the results of Dobreanu *et al.* (1988) ranged between 13·9% and 15·8%.

For the percentage of individual sugars, sucrose and glucose were always the highest, ranging from 2% to 6%. Except for the cultivar Tardicotes, which has a high amount of this sugar, fructose ranged from 0·76% in Sel D5 (BO) to 3·6% in Prugna d'Argento (FO). The data reported by Wrolstad and Shallenberger (1981) showed, for the three sugars examined, similar ranges to ours.

In both the two dark and light colour samples of the cultivar Tardicotes, the amount of sucrose was very low with respect to the other cultivars, while the fructose was higher. Considering that this cultivar also showed a high ripeness index, this sugar pattern could be due to the presence of invertase, which causes a marked decrease in sucrose content at the overripe stage (Buchloch & Neubeller, 1969).

The amount of sorbitol (fr.wt) ranged from 1% in BlueFre (RO) to 5·33% in Sel D8 (BO) dark with a %

Table 3. Sorbitol content of different fruits

	Apple(1)	Pear(2)	Plum(3)	Prune(4)	Peach(5)	Apricot(6)
Range* (% fr.wt)	0·20–0·75	1·21–2·83	0·62–2·60	9·40–13·9	0·03–0·47	0·05–0·46
Mean* (% fr.wt)	0·44	2·12	1·66	13·9	0·19	0·36
SD	0·29	0·59	0·76	3·63	0·14	0·17
% CV	67·6	27·7	46·1	26·2	73·5	49·0

The mean and statistical values are calculated from the data of:

(1,2,3) Richmond *et al.* (1981); Wrolstad and Shallenberger (1981).
(4) Wrolstad and Shallenberger (1981).
(5) Bassi and Selli (1990); Wrolstad and Shallenberger (1981).
(6) Bassi and Selli *et al.* (1990).
* % on fresh weight.

Table 4. Sorbitol percent on total sugars plus sorbitol

	Apple(1)	Pear(2)	Plum(3)	Prune(4)	Peach(5)	Apricot(6)
Range	1·50–9·43	9·70–23·6	6·61–22·9	19·0–28·3	0·55–5·50	0·74–6·05
Mean	4·74	17·6	16·6	24·4	2·32	3·94
SD	2·71	4·37	6·24	4·22	1·61	1·97
% CV	57·2	24·8	39·0	17·4	69·6	50·1

The mean and statistical values are calculated from the data of:

(1,2,3) Richmond *et al.* (1981); Wrolstad and Shallenberger (1981).
(4) Wrolstad and Shallenberger (1981).
(5) Bassi and Selli (1990); Wrolstad and Shallenberger (1981).
(6) Bassi and Selli *et al.* (1990).

CV of 34·9%. There is about as much sorbitol present in plums as in fructose. Hartmann (1984) analysed 36 cultivars of plums from different origins over a period of six years and placed the cultivars in three groups according to their sorbitol content on dry weight: low sorbitol plums, ranging from 0·2 to 5·6%; medium sorbitol plums, from 3·3 to 6%; and high sorbitol plums, from 6·6 to 35·1%. The cultivars considered in this research belong to the last group. The sorbitol calculated as a percentage of total sugars plus sorbitol ranged from 9·33 in BlueFre (RO) to 26·61% in Sel D8 (BO) dark, with a % CV lower than the one reported by Wrolstad and Shallenberger (1981) (19·9 and 39% respectively).

In agreement with Hartmann (1984), no relation was found between the sorbitol and sucrose contents of plums, while Hartmann's observation that cultivars with a high sugar content also contain much more sorbitol were confirmed by the calculation of the linear regression, on 16 of the plums tested, between sorbitol and total sugars (R^2 = 71·51% ; $Y = 0{\cdot}41X - 1{\cdot}86$).

Tables 3 and 4 show the statistical calculations, on data compiled from the literature, including the range, mean, standard deviation and % CV of the sorbitol content of different fruits. Plums and apples show the highest amounts of sorbitol. In dried plums (prunes) sorbitol is 25% of the total sugars and sugar alcohols. Our cultivars contained much more sorbitol than those reported in the literature, ranging from 1 to 5·33% compared with 0·62 to 2·60%, respectively. The mean of the sorbitol, calculated as a percentage of total sugars plus sorbitol, was 19·3% for the plum tested, whereas those calculated from literature data for plums and pears were 16·6% and 17·6%.

CONCLUSION

Our results confirm that the glucose/fructose ratio can be considered as a taxonomic feature for plums and that the sorbitol content is directly related to the total sugar content.

The high sorbitol content of the cultivars tested is important in drying because the sugar alcohols do not undergo Maillard degradation, so the prune colour is prevented from excessive browning. Furthermore, sorbitol acts as an 'antidrying agent' (Zimmermann, 1989), since it enables one to obtain dried products with higher humidity but with the same water activity, so the cultivars tested could be particularly suitable for the production of good quality prunes. The sorbitol content should be taken into account together with other criteria of plum suitability for drying processing. Acidity and sugar contents agreed with the literature data.

By using a Polypore Pb polymeric column, sorbitol can be adequately separated, in a simple procedure, from glucose, in the presence of fructose and sucrose. The application of this chromatographic system to the sugars and sorbitol analysis of plums enabled us to characterise the sugar pattern of some cultivars grown in Italy, confirming the results of earlier work (Wrolstad & Shallenberger, 1981; Hartmann, 1984) made on other cultivars grown in different areas.

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