

## Patterns of Barley Grain Development in Spain and Scotland and Their Implications for Malting Quality

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### ABSTRACT

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To determine whether patterns of grain filling were consistent between seasons and different between sites in northern and southern Europe, the cultivar Troubadour and TR49, a mutant derived from it, were grown, over two seasons, at sites in Scotland and northern Spain. Differences in sowing date and climate were reflected in different patterns of grain filling. Ear emergence in Scottish grown barley occurred around the time when daylight hours were maximal; optimal photosynthesis was the likely explanation for the rapid increase in grain size observed at the Scottish site. Differences between the sites in temperature and rainfall were most evident during the last month of the growing season. In Scotland, where ripening occurred in cooler, more humid conditions, synthe-

sis of hordein and  $\beta$ -glucan followed the pattern of grain filling, reaching a peak at ~600 degree days after anthesis (the product of days after anthesis and average temperature). Levels then remained fairly constant until harvest ripeness was reached. In Spain, levels of hordein and  $\beta$ -glucan rose virtually throughout the growing season. Differences observed at maturity, between Scottish and Spanish grown grain, in total nitrogen and  $\beta$ -glucan levels were due to this accumulation in the later stages of growth. This was accompanied by a major change in the ratio of the constituent polypeptides of the storage protein and differences in the relative proportions of soluble and insoluble  $\beta$ -glucan.

The genotype TR49 was one of several mutants derived from the cultivar Troubadour, by selection for a faster rate of germination (Molina-Cano et al 1989). Although it was shown to be of superior malting quality when compared with its parent, over a range of Spanish sites (Molina-Cano et al 1993), differences between cultivars were much less than those between diverse environments (Molina-Cano et al 1995, Swanston et al 1995). There were differences between Spanish and Scottish grown grain in  $\beta$ -glucan and nitrogen contents, while the relative proportions of the component polypeptides of the main storage protein also varied (Swanston et al 1993b, Molina-Cano et al 1995). Spanish grown grain showed a more rapid and extensive enzyme synthesis during germination (Swanston et al 1995), which may be associated with the higher levels of  $\beta$ -glucanase detected in the mature grain (Ellis et al, *in press*). Consequently, although  $\beta$ -glucan content of the endosperm cell walls was higher in Spanish as compared to Scottish grown grain, there was a greater degree of  $\beta$ -glucan degradation during malting in the Spanish samples. Cell-wall modification was only a limiting factor in malting of these cultivars when grown in Scotland.

These data suggested that not only were environmental effects influencing quality, but that different mechanisms to promote malting quality may be operating in the two diverse environments. Molina-Cano et al (1995) suggested that to use parameters to assess quality in a Spanish environment similar to those used in north-western Europe (i.e., low levels of nitrogen and  $\beta$ -glucan) could be misleading. A new definition would require consideration of the relative amounts of components of both storage protein and cell walls.

Morgan and Riggs (1981) suggested that levels of  $\beta$ -glucan, especially soluble  $\beta$ -glucan, were increased in hotter, drier environments, but their work was restricted to sites within the United Kingdom. In addition, MacNicol et al (1993) suggested that the precise timing of a stress factor, rather than the factor itself, may be the critical determinant of the effect. The same authors also demonstrated that the effect on malting performance may not always be

predicted from measurements on grain components, as grain stressed by drought in the late grain-filling period showed no change in  $\beta$ -glucan or nitrogen level, but an increase in hot water extract.

Recent studies on effects of heat or drought on malting quality (MacNicol et al 1993, Savin and Nicolas 1996) have made use of controlled environments. One potential problem of this approach is that it cannot take into account any variation in conditions prior to the period of stress that could be experienced by a field crop. For example, the root development of barley sown into a damp seed bed may be different from that occurring under drier conditions. This may influence the subsequent response of the crop to an extended period of drought.

In this article, we consider two widely diverse sites and include data from contrasting seasons. The aim is to determine whether patterns of grain filling are consistent between seasons and whether these patterns clearly differ between sites in northern and southern Europe. As a result, a clearer understanding of the influence of differing environmental conditions on grain texture and composition and how these affect malting performance may be gained. Such information will be of importance in defining the optimal cultivars and husbandry practices (e.g., sowing date) to ensure the production of good malting quality barley across a wider area of the EU than is possible at present.

### MATERIALS AND METHODS

It had been decided to investigate the changes occurring during grain filling, as a possible means of understanding the differences between mature grain of the two genotypes Troubadour and TR49. In 1991, these genotypes, grown in Scotland (Swanston et al 1993a), had shown differences in grain size, nitrogen content, and milling energy, a measure of the mechanical energy required to disrupt the endosperm structure (Allison et al 1979). Differences between the two genotypes in Spain were much less evident (Swanston et al 1993b). In addition, it was possible to determine differences in dormancy on grain grown in Scotland (Swanston et al 1993a), so the Scottish site was chosen for a pilot study in 1992.

Both genotypes were included in a trial of two replicates, grown at the Scottish Crop Research Institute (SCRI), Dundee. Plots were 2 m long and 1.5 m wide. During the growing season, ears were harvested from the plots, at twice-weekly intervals, and dried as described by Riggs and Gothard (1976). Sampling com-

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menced 14 days after anthesis and continued until six weeks after anthesis to ensure that the main grain-filling period was fully encompassed (Walpole and Morgan 1971, Riggs and Gothard 1976).

The following season, trials were sown at both SCRI and at Bell-Lloc, Lleida, Spain. Sampling in Scotland was again undertaken as described above, with the exception that it was continued until harvest. In Spain, sampling was undertaken at similar intervals until harvest, but commencing six days after anthesis. In 1994, a trial was sown at Lleida to give a second season's data from Spain.

Grain collected during the growing season was assessed for 1,000 kernel weight (TKW) and milling energy (Allison et al 1979). The volume occupied by 5-g samples of very light grain from early sampling dates could not be accommodated in the mill hopper, so sample size was reduced to 1 g, with measurements done in triplicate to ensure accuracy. Total hordein content and B-to-C hordein ratio were determined on barley flour by the method of Griffiths (1987). Total and insoluble  $\beta$ -glucan contents were determined by an enzymic method (McCleary and Glennie-Holmes 1985) after extraction as described by Åman and Graham (1987). Following harvest, grain retained by a 2.5 mm sieve was malted according to the regime described by Molina-Cano et al (1989). The European Brewery Convention (EBC) recommended methods of analysis (EBC 1975) were used to determine extract, total malt nitrogen, Kolbach index, apparent attenuation, and wort viscosity.

Because spring cultivars of barley are sown in autumn in Spain, conventional site versus year comparisons were difficult. This was overcome by presenting data collected on developing grain against

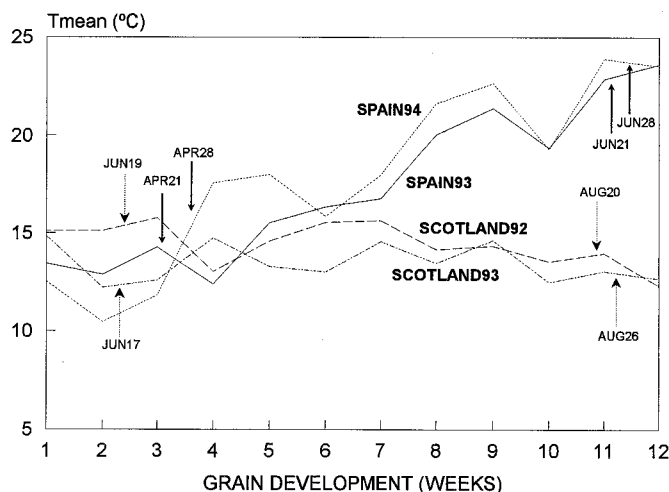
a scale of degree days after anthesis, this being the product of days after anthesis and average daily temperature (Molina-Cano et al 1996).

Analysis of variance (ANOVA) was performed using the SAS package PROC GLM as previously described (Molina-Cano et al 1995). Curves were fitted to the grain development data graphs using version 2.03 of TableCurve (Jandel Corporation, San Rafael, CA).

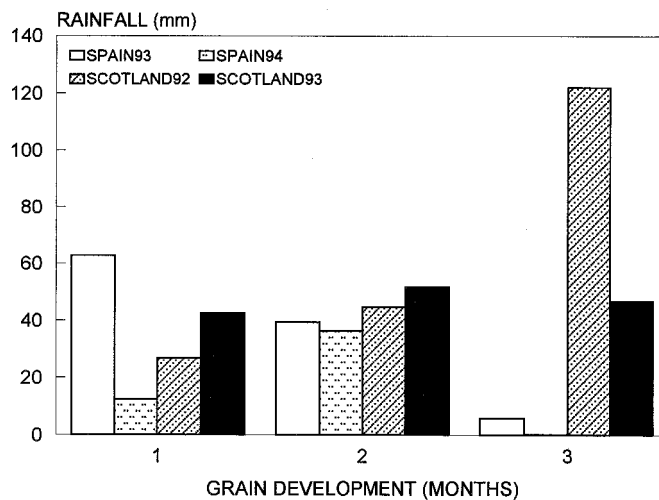
## RESULTS

### Climatic Differences

Ear emergence of spring barley in the Dundee, Scotland, area generally occurs in June, while Spanish grown barley will reach ear emergence in April. Mean daily temperatures over the period from emergence to harvest were therefore presented over a 12 week period rather than on the basis of calendar months (Fig. 1), to enable comparison between both sites and years. The daily temperature in Scotland at the time of ear emergence in 1992 was higher than that in the following year, and temperatures in Dundee in mid-June were not widely different from those observed in Lleida in mid-April (Fig. 1). In Scotland, however, mean daily temperatures show little variation throughout the grain-filling period, while in Spain, there is a marked increase, with maximum temperatures being observed around the time of harvest. There were seasonal fluctuations in rainfall at both sites (Fig. 2), but the biggest differences between the Scottish and Spanish sites were observed during the last few weeks before harvest. In both seasons, Spanish grain was harvested during a very dry spell. Low temperatures at harvest ripening and a slow rate of desiccation are factors that increase the risk of dormancy (Stowell 1987), so cli-



**Fig. 1.** Mean weekly temperatures (°C) during grain development in Scotland (1992 and 1993) and Spain (1993 and 1994). Anthesis and maturity dates are indicated by solid arrows in Spain and dashed arrows in Scotland. Periods of grain development were April through June (Spain) or June through August (Scotland).



**Fig. 2.** Monthly rainfall (mm) during grain development in Scotland (1992 and 1993) and Spain (1993 and 1994).

**TABLE I**

Analyses of Variance<sup>a</sup> for 1,000-Kernel Weight (TKW), Total and Insoluble  $\beta$ -Glucans, Total Hordein, B-to-C Hordein Ratio, and Milling Energy During Grain Development of Two Near-Isogenic Barley Genotypes in Scotland (1992 and 1993) and Spain (1993 and 1994)

Source of Variation	DF <sup>b</sup>	TKW (g)	$\beta$ -Glucan (%)		Hordein		Milling Energy (J)
			Total	Insoluble	Total <sup>c</sup>	B-to-C Ratio	
Environment	3	56.9*** <sup>d</sup>	1.1*	0.5	25,650.2*	2.49**	319.3
Genotype	1	16.4***	0.0	0.0	2,777.3	0.13	13.1
Environment $\times$ genotype	3	4.3**	0.1	0.2	2,809.4	0.00	0.9
Development stage	1	7,548.1***	49.4***	20.1***	2,526,828.2***	2.96**	11,561.6***
Environment $\times$ development stage	3	6.1***	1.1*	0.4	48,047.2**	1.06**	630.0*
Genotype $\times$ development stage	1	4.4***	0.0	0.0	308.0	0.02	12.4
Error	3	0.02	0.1	0.2	1,723.4	0.03	40.6
Total	15						

<sup>a</sup> Mean squares.

<sup>b</sup> Degrees of freedom.

<sup>c</sup> Arbitrary units.

<sup>d</sup> Significance level: \*, \*\*, \*\*\* = 0.05, 0.01, and 0.001, respectively.

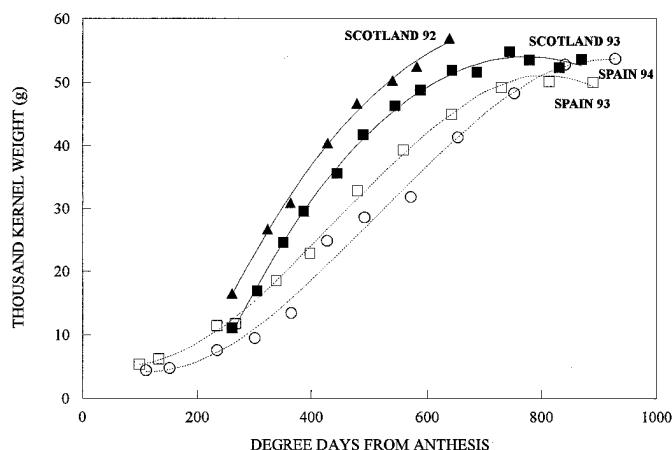
matic differences between the Scottish and Spanish sites in the weeks immediately prior to harvest may explain dormancy differences observed previously (Swanston et al 1993a).

### Grain Size and Texture

Of all the parameters measured on developing grain, only TKW showed any significant differences between genotypes or genotype by environment interaction (Table I). This supported previous data from mature grain (Swanston et al 1993b), where TR49 only demonstrated a significant increase over Troubadour under Scottish growing conditions. It was therefore decided that differences between sites, seasons, and sampling dates could be based on the pooled data from the two cultivars.

The development of TKW in Scotland (Fig. 3) was similar to the pattern observed by Riggs and Gothard (1976), with a period of rapid accumulation, terminating at about 600 degree days after anthesis. In 1993, TKW remained fairly constant until harvest. In Spain, the period of rapid growth commenced about the same time (i.e., 250–300 degree days), but continued until ~800 degree days. On the scale of degree days after anthesis, harvest ripeness showed little difference between years in Spain or between Scotland and Spain in 1993.

The rate of increase in TKW varied between years at both sites but clearly followed a definable curve in all instances, with regression equations explaining 99% of the variation. The increase was always more rapid between 400 and 600 degree days in Scotland. This period was not coincident with the largest climatic variation, but it did coincide with day length differences between sites. Ear emergence occurred around the time of maximum day length at Dundee and this, coupled with the more northerly latitude, would ensure a considerably longer day length for a most of the main grain-filling period. This should enhance photosynthesis, enabling starch synthesis to be more extensive, and lead to higher TKW.



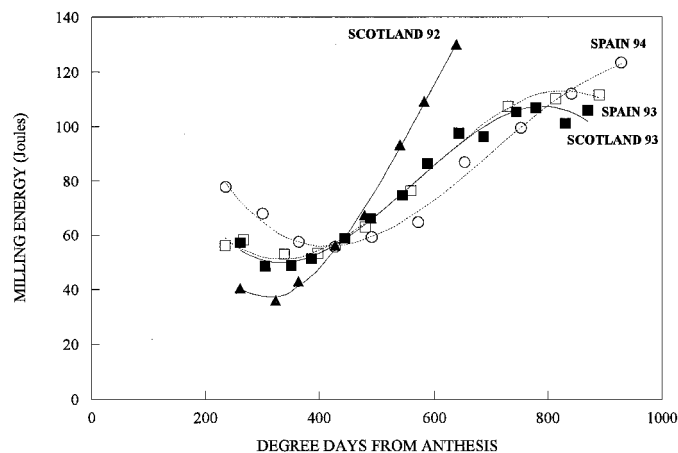
**Fig. 3.** Changes in 1,000-kernel weights during grain development in Scotland and Spain. Data are means of two barley genotypes, Troubadour and TR49. Curves for the four environments are given by the following equations. Scotland: 1992,  $y = -40.59 + 0.27x - 1.9 \times 10^{-4}x^2 + 1.98 \times 10^{-8}x^3$  ( $r^2 = 0.99$ ); 1993,  $y = -48.76 + 0.28x - 2.0 \times 10^{-4}x^2 + 2.12 \times 10^{-8}x^3$  ( $r^2 = 0.99$ ). Spain: 1993,  $y = 6.81 - 0.04x + 3.1 \times 10^{-4}x^2 - 2.33 \times 10^{-7}x^3$  ( $r^2 = 0.99$ ); 1994,  $y = 7.41 - 0.06x + 2.9 \times 10^{-4}x^2 - 1.91 \times 10^{-7}x^3$  ( $r^2 = 0.99$ ).

Milling energy development also followed well-defined curves (Fig. 4), but these did not match the patterns of grain filling. The initial decline in milling energy was due to the reduced contribution of the husk, which is the most fibrous and resistant to milling of the barley tissues (Camm et al 1990). The main period of increase began ~400 degree days after anthesis, which was near the mid-point of the main grain-filling period in Scotland (Fig. 3). In Scotland, milling energy continued to increase after the main grain-filling period had ended (~800 degree days) (Fig. 4). Differences between years were observed at both sites, but there was no difference in the pattern of milling energy development between Dundee and Lleida in 1993. Differences between years in rates of increase were most apparent after 500 degree days, the convergence of milling energies at the Spanish site being the preliminary to a change in the relative ranking between seasons.

### Total and Insoluble $\beta$ -Glucan

Comparison of Scottish and Spanish sites for total  $\beta$ -glucan synthesis in 1993 (Molina-Cano et al 1996), suggested that Scottish grown barley followed a pattern similar to that observed in eastern England by Smith et al (1987). Synthesis continued until approximately six weeks after anthesis with levels then fairly constant until harvest ripeness. By contrast, total  $\beta$ -glucan levels in Spain rose virtually throughout the period from anthesis to harvest. Data from Spain in 1994 (Fig. 5A) suggested a similar pattern between seasons. The level of total  $\beta$ -glucan in Dundee at the end of the main grain-filling period did, however, show rather more variation between seasons, being lower in 1992 than in 1993. These results were reflected in the significant difference between environments in ANOVA (Table I).

Morgan and Riggs (1981) suggested that the increase in  $\beta$ -glucan, associated with hotter, drier environments, was particularly evident in the soluble portion. Here, the lowest levels of insoluble  $\beta$ -



**Fig. 4.** Changes in milling energy during grain development in Scotland and Spain. Curves for the four environments are given by the following equations. Scotland: 1992,  $y = 216.57 - 1.33x + 2.9 \times 10^{-3}x^2 - 1.67 \times 10^{-6}x^3$  ( $r^2 = 0.99$ ); 1993,  $y = 183.07 - 0.93x + 2.0 \times 10^{-3}x^2 - 1.18 \times 10^{-6}x^3$  ( $r^2 = 0.99$ ). Spain: 1993,  $y = 167.59 - 0.81x + 1.7 \times 10^{-3}x^2 - 9.84 \times 10^{-7}x^3$  ( $r^2 = 0.99$ ); 1994,  $y = 210.44 - 0.87x + 1.5 \times 10^{-3}x^2 - 7.07 \times 10^{-7}x^3$  ( $r^2 = 0.99$ ).

**TABLE II**  
Mean Values of the Malting Quality Parameters Measured on Two Near-Isogenic Barley Genotypes in Scotland (1992 and 1993) and Spain (1993 and 1994)<sup>a</sup>

Site and Year	Malt Extract (%)	Malt Total Protein (%)	Kolbach Index	Apparent Final Attenuation (%)	Wort Viscosity (cST)
Scotland, 1992	80.15a	9.49c	41.55b	79.95b	1.80b
Scotland, 1993	80.41a	8.00d	46.05a	78.39b	2.13a
Spain, 1993	78.82b	12.25b	34.53c	80.28a	1.63b
Spain, 1994	75.56b	15.02a	28.74d	77.90b	1.65b

<sup>a</sup> Means followed by the same letter in the same column are not significantly different at the 0.05 level.

glucan (Fig. 5B) were observed in Spain in 1994, which was the driest of the four environments studied (Fig. 2). There was little difference between the levels of insoluble  $\beta$ -glucan, synthesized during the main grain-filling period in 1992 and 1993 at the Scottish site, probably reflecting the relative similarities of temperature (Fig. 1) and rainfall (Fig. 2).

### Hordein Content and Composition

In 1993, total hordein composition followed a similar pattern of development to total  $\beta$ -glucan. In Scotland, there was rapid accumulation until ~600 degree days after anthesis (Fig. 6A), then levels remained fairly constant until harvest ripeness. By contrast, in Spain, levels continued to rise throughout the period until harvest. Differences in grain nitrogen levels between Spanish and Scottish grown grain (Swanston et al 1993b, Molina-Cano et al 1995) are probably due to this accumulation of storage protein in the later stages of grain maturation. Although there appeared to be differences between seasons at both sites in the rate of hordein accumulation (Fig. 6A), patterns of accumulation were site-specific. Higher levels of hordein were observed in Spanish grown grain as a result of accumulation for a greater proportion of the growing season.

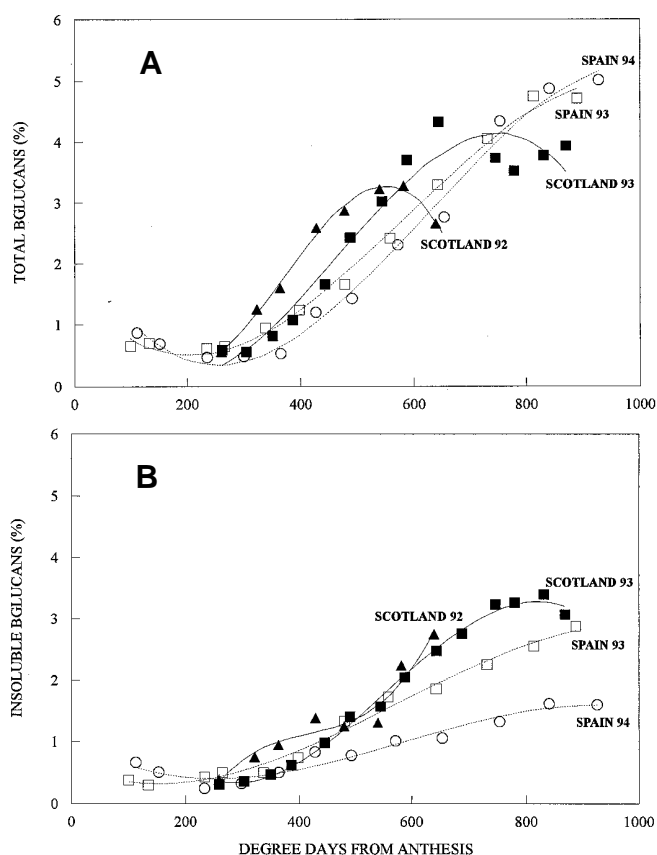
There were also major differences between the sites in the pattern of B-to-C hordein ratio (Fig. 6B). At both sites, the highest values were recorded between 300 and 400 degree days after anthesis. In Scotland, there was only a slight subsequent decline in the ratio, but values in Spain fell very rapidly towards harvest ripeness.

Consequently, mature Spanish grown grain had a much lower B-to-C hordein ratio than Scottish grown grain. Griffiths (1987) suggested that lower B-to-C hordein ratios were associated with higher levels of grain nitrogen, but significant changes in B-to-C hordein ratio have not previously been observed during the later stages of grain filling. The decline in B-to-C hordein ratio in Spain from ~350 degree days until maturity was linear in both seasons, but attempts to fit straight lines to the decline in B-to-C hordein ratio in Scotland were less successful. This was particularly evident in 1993, when the entire period to harvest ripeness was considered and only 35% of variation was explained.

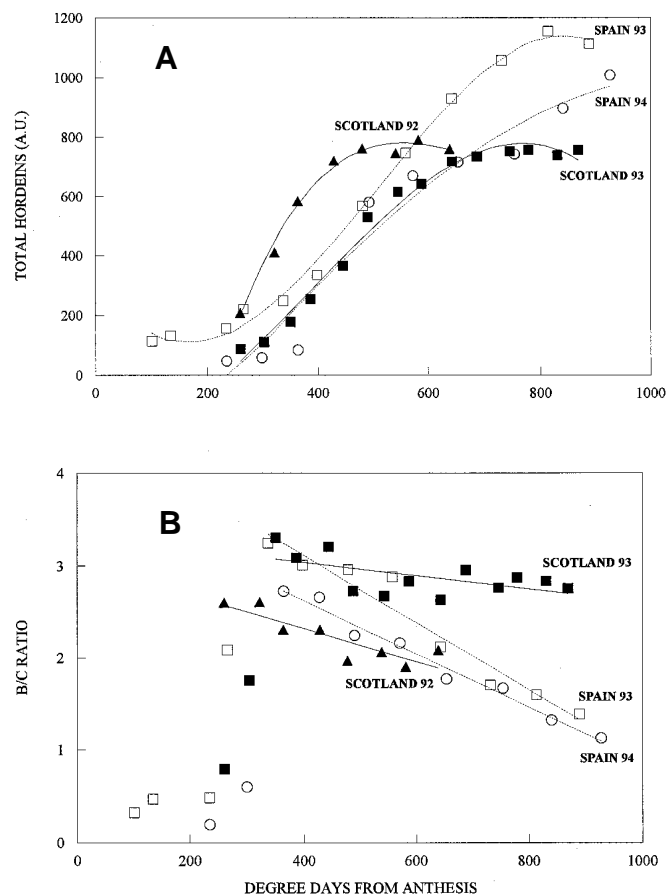
### Malting Analyses

The higher levels of  $\beta$ -glucan observed in the developing grain were not reflected in wort viscosities. Values for the Spanish grown grain from both seasons were equal to or significantly lower than those of grain grown in Scotland (Table II). This is most likely due to the more rapid and extensive synthesis of  $\beta$ -glucanase observed under Spanish conditions (Swanston et al 1995).

Spanish grown grain had much higher levels of total malt protein than did Scottish grown grain, but there were also differences between years in Spain (Table II). This did not correspond with total hordein data during grain filling, which was higher in 1993. Synthesis of other proteins may have been enhanced in Spain in 1994, which was the warmest and driest of the environments studied. Total protein had an effect on extract yield and Kolbach



**Fig. 5.** Changes during grain development, in Scotland and Spain, in total (A) and insoluble (B)  $\beta$ -glucan. Curves for the four environments are given by the following equations. A, Scotland: 1992,  $y = 3.37 - 0.04x + 1.3 \times 10^{-4}x^2 - 1.23 \times 10^{-7}x^3$  ( $r^2 = 0.99$ ); 1993,  $y = 1.80 - 0.02x + 6.33x^2 - 4.51 \times 10^{-8}x^3$  ( $r^2 = 0.94$ ). Spain: 1993,  $y = 1.64 - 0.01x + 3.56x^2 - 2.03 \times 10^{-8}x^3$  ( $r^2 = 0.99$ ); 1994,  $y = 2.49 - 0.02x + 4.53x^2 - 2.42 \times 10^{-8}x^3$  ( $r^2 = 0.99$ ). B, Scotland: 1992,  $y = -7.84 + 0.06x - 1.3 \times 10^{-4}x^2 + 1.10 \times 10^{-7}x^3$  ( $r^2 = 0.95$ ); 1993,  $y = 3.85 - 0.03x + 0.6 \times 10^{-4}x^2 - 3.90 \times 10^{-8}x^3$  ( $r^2 = 0.99$ ). Spain: 1993,  $y = 0.61 - 3.9 \times 10^{-3}x + 1.0 \times 10^{-5}x^2 - 8.69 \times 10^{-9}x^3$  ( $r^2 = 0.99$ ); 1994,  $y = 1.04 - 0.06x + 1.0 \times 10^{-5}x^2 - 7.98 \times 10^{-9}x^3$  ( $r^2 = 0.95$ ).



**Fig. 6.** Changes during grain development, in Scotland and Spain, in total hordein content (A) and B-to-C hordein ratio (B). Curves for the four environments are given by the following equations. A, Scotland: 1992,  $y = -2053.4 + 13.14x - 0.02x^2 + 9.47 \times 10^{-6}x^3$  ( $r^2 = 0.99$ ); 1993,  $y = -199.3 - 0.12x + 5.3 \times 10^{-3}x^2 - 4.50 \times 10^{-6}x^3$  ( $r^2 = 0.99$ ). Spain: 1993,  $y = 327.6 - 2.81x + 0.01x^2 - 6.58 \times 10^{-6}x^3$  ( $r^2 = 0.99$ ); 1994,  $y = -543.5 + 2.24x - 8.1 \times 10^{-4}x^2 - 6.20 \times 10^{-7}x^3$  ( $r^2 = 0.95$ ). B, Scotland: 1992,  $y = 3.04 - 1.8 \times 10^{-3}x$  ( $r^2 = 0.77$ ); 1993,  $y = 3.33 - 7.2 \times 10^{-4}x$  ( $r^2 = 0.35$ ). Spain: 1993,  $y = 4.57 - 3.7 \times 10^{-3}x$  ( $r^2 = 0.94$ ); 1994,  $y = 3.78 - 2.9 \times 10^{-3}x$  ( $r^2 = 0.98$ ).

index, as the environments followed the same ranking order for all three characters. Protein modification and extract were both reduced in Spain. By contrast, the high Kolbach index figures for the Scottish grown samples suggested a degree of over-modification of the malt, although sufficient cell wall material remained to give high wort viscosity figures. The high Kolbach index of the Scottish grown samples meant that the actual quantity of protein in solution was fairly similar between sites and seasons, while the release of starch-derived material to the growing embryo would be increased due to breakdown of the protein matrix surrounding the starch granules. This was reflected in the fact that Scottish samples did not have higher attenuation figures despite higher extracts.

## DISCUSSION

Rahman et al (1982) suggested that the relative proportion of C hordein is highest in young endosperm and falls until ~26 days after anthesis. It then remains fairly constant until maturity. Allowing for the differences in technique used, this pattern could fit the data points observed here for Scottish grown grain in 1993, where the B-to-C ratio declined until ~500 degree days and then leveled off until harvest. The pattern noted by Rahman et al (1982), however, is clearly very different from that observed in Spain.

Sulfur deficiency can alter the ratio of B-to-C hordein (Rahman et al 1983) as it affects both the transcription and the translation of mRNAs. Translation of B hordein mRNA is decreased, while that of C hordein is enhanced under low sulfur conditions. Information on the soil mineral status of the fields used in this experiment is not available, but this will be one area of future investigation.

The sulfur rich B and D hordeins are the major components of gel protein, thought to have a deleterious effect on malting quality (Smith and Simpson 1983). There is, however, some debate as to which of the hordein polypeptides are most implicated in reducing quality. Skerritt and Janes (1992) observed an elevation of B1 and B2 hordein subunits in samples of poor malting quality, but Benetrix et al (1994) suggested that increased amounts of C hordeins limited water diffusion during the steeping phase of malting and quality was impaired.

Here, the samples follow the pattern suggested by Griffiths (1987) in that increasing B-to-C hordein ratios across the four sites are associated with higher nitrogen levels. It is not possible to dissect the effects of nitrogen content and polypeptide composition. However, the changes in B-to-C ratio during grain filling, in the Spanish samples suggest that polypeptide composition may vary across the endosperm, with a higher proportion of C hordein in the younger cells. A closer study of the rates and patterns of modification during malting may be of considerable value. In addition, there is need to consider a wider range of cultivars and to examine factors such as soil mineral status and nutrient uptake by the plants. In particular, the balance between nitrogen and sulfur may be critical and this could be altered by cultural practice. A fuller understanding is necessary to enable conclusions on the wider production of malting barley.

## CONCLUSIONS

For the genotypes studied here, the following conclusions may be drawn. First, Scottish grown spring barley emerged around the period of maximum day length and appeared to show more rapid early grain filling than autumn sown Spanish samples, emerging in late spring. Second, Spanish grown grain ripened in much hotter and drier conditions than Scottish grown grain, with  $\beta$ -glucan and hordein accumulating throughout the period up to harvest, giving higher levels than in Scotland.

High  $\beta$ -glucan levels were not problematic, probably due to rapid and extensive production of  $\beta$ -glucanases during malting. Initial  $\beta$ -glucan degradation may also have been assisted by  $\beta$ -glucanases synthesized in the developing grain and detected at

maturity (Ellis et al, *in press*). It is possible that hot temperatures immediately before harvest in Spain resulted in rapid grain maturation, leaving a residue of enzymes.

Finally, Spanish grown barley can produce very high protein levels, especially in hotter, drier seasons. This can lead to under-modification of the endosperm during malting and low levels of extract yield. Different patterns of endosperm modification seem to operate in the two environments. Once there is sufficient cell-wall breakdown to permit access of other enzymes, Scottish grown grain exhibits extensive protein solubilization. In Spain, however, although cell-wall modification is very rapid, breakdown of the protein matrix surrounding the starch granules appears to be a limiting factor.

## ACKNOWLEDGMENTS

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