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SURFACE WAXES FROM SEEDS OF *HORDEUM VULGARE*

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Key Word Index—*Hordeum vulgare*; Gramineae; seed waxes; β-diketones; hydrocarbons; esters; free acids; free alcohols.

Abstract—The main components present in *Hordeum vulgare* ssp. *distichum* cv. Fairfield and ssp. *hexastichum* cv. Klondike seed waxes are described. The principal constituents in the *distichum* subspecies include hydrocarbons and esters with a small percentage of β-diketones. β-Diketones, however, are the main components of the subspecies *hexastichum* wax.

INTRODUCTION

Hordeum vulgare leaf waxes have been extensively studied [1–4], while the chemistry of their seed waxes has received much less attention. In this paper we report on the composition of the seed waxes from two subspecies, *distichum* and *hexasticum*.

RESULTS AND DISCUSSION

The wax on *H. vulgare* ssp. *distichum* represents 0.23% of the dry wt of the seeds, while for ssp. *hexastichum* the figure is 0.20%. By a combination of prep. TLC and GC [5, 6] methods the waxes were separated into various fractions (Table 1). The composition of these fractions was then determined. Hydrocarbons, esters, β-diketones, alkanols, acids and hydroxy-β-diketones are present in both subspecies, but the proportions vary greatly. (Tables 2 and 3). The wax from ssp. *distichum* seeds has a pattern which is similar to that of other seeds, i.e. the main fractions being hydrocarbons, esters and free acids, with the presence of other constituents, including β-diketones [5–9]. However, the wax from ssp. *hexastichum* has a high percentage of β-diketones, something unusual in Gramineae seeds, and only described for Gramineae in the leaf wax of *Agropyron intermedium* and *A. smithii* [10, 11]. Hydrocarbons, esters and alkanols are minor constituents in this subspecies.

The hydrocarbon fractions in the two subspecies have similar distribution patterns, which are similar to those observed in the Bonus and Foma *Hordeum* lineages [2, 4]. There are marked differences in the composition of free acids which have a more extended range in ssp. *distichum* and show some unsaturation; the latter has been related to higher drought tolerance [11, 12]. The main alkanol is hexacosanol in both subspecies, but in *distichum* there is a more extended range of homologues including 2-pentadecanol. The alkanols in ssp. *hexastichum* do not include secondary alcohols, an unusual situation for waxes with a high percentage of diketonic constituents. A similar situation exists in *H. vulgare* cer-t 46 mutant [3]. The diketones are those already described for *H. vulgare* [1, 13]. The hydroxy-β-diketones are a mixture of 25- and 26-hydroxy isomers. Aldehydes [14] and ketones [15] which were previously described for *H. vulgare*, could not be detected.

Table 1. Fractions of *H. vulgare* ssp. *distichum* and ssp. *hexastichum* seed waxes

Fraction	ssp. *distichum**	ssp. *hexastichum**
Hydrocarbons	25.0	1.5
Esters	11.0	0.5
Free alcohols	4.6	1.0
Free acids	16.1	11.0
β-Diketones	27.0	34.0
Hydroxydiketones	8.0	38.0

*w/w% as determined following methodology of ref. [5].

Table 2. Composition of *H. vulgare* ssp. *distichum* seed wax (wt% as determined by GC)

Carbon	Hydrocarbons	Esters		Free alcohols	Free acids
		Alcohols	Acids		
14	—	—	15.8	—	10.2
15	—	18.2(2-ol)		—	—
16:1	—	—	12.0	—	—
16	—	8.8	30.6	—	37.7
18:1	—	—	10.2	—	6.2
18	—	—	7.6	—	6.2
20	—	2.5	6.3	—	4.8
21	3.2	—	—	—	—
22	tr	5.0	10.9	—	5.8
23	3.2	—	—	—	2.0
24	1.0	7.9	10.9	15.3	1.5
25	7.3	—	—	—	1.0
26	tr	18.5	3.6	36.4	21.9
27	7.6	1.5	1.1	—	—
28	7.3	7.5	1.8	15.8	2.3
29	22.8	—	—	—	—
30	1.0	16.5	—	28.7	1.9
31	42.2	—	—	—	—
32	3.2	—	—	—	1.3

14,16-Hentriacontandione is 98% of the β-diketone fraction. 25-Hydroxy-14,16-hentriacontandione is 70% and 26-hydroxy-14,16-hentriacontandione 30% of the hydroxy-β-diketone fraction.

Table 3. Composition of *H. vulgare* ssp. *hexastichum* seed wax (wt% as determined by GC)

Carbon	Hydrocarbons	Esters		Free alcohols	Free acids
		Alcohols	Acids		
16	—	—	36.5	—	6.9
18	—	—	18.2	—	1.2
20	—	—	6.3	—	34.4
22	—	—	2.7	—	27.5
23	0.8	—	—	—	—
24	—	24.6	—	14.7	—
25	4.3	—	—	—	—
26	0.1	58.7	—	60.5	—
27	11.1	–	–	–	–
28	—	14.4	—	14.8	—
29	28.5	—	—	—	—
30	1.7	—	—	—	—
31	41.0	—	—	—	—
32	tr	—	—	—	—
33	4.6	—	—	—	—

14,16-Hentriacontandione is 95% of the β-diketone fraction. 25-Hydroxy-14,16-hentriacontandione is 90% and 26-hydroxy-14,16-hentriacontandione 10% of the hydroxy-β-diketone fraction.

EXPERIMENTAL

Mature seeds of *H. vulgare* ssp. *hexastichum* cv. Klondike and ssp. *distichum* cv. Fairfield were obtained from the NRCC Prairie Regional Laboratory (Dr A. P. Tulloch). The waxes were extracted from the seed surface by immersion (15 sec) in $CHCl_3$. Waxes were analysed and quantified by TLC and GC methods described elsewhere [5, 6]. The wax from ssp. *hexastichum* was also fractionated by CC. Total β-diketones were determined by UV measurement at 273 nm and visualized by development of the TLC plates with Fast Blue B salt [19]. 14,16-Hentriacontandione was identified by MS (*m/z* 464, 446, 281, 278, 253, 250, 239, 220, 211, 192, 138, 100, 43 (base peak) [11]. Hydroxydiketones were also identified by MS (typical peaks at *m/z* 408 and 395) [11] and the relative abundance by GC of the Me esters of the acids obtained by hydrolysis [10, 11].

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