Phytochemistry, Vol. 27, No. 2, pp. 373–375, 1988.
Printed in Great Britain.

0031-9422/88 $3.00+0.00

VOLATILE AROMA CONSTITUENTS OF CELERY

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(*Received* 5 *February* 1987)

Key Word Index—*Apium graveolens*; Umbelliferae; celery; aroma volatiles.

Abstract—The aroma volatiles of a local variety of celery from Libya were analysed using routine procedures. Nine of the identified components have not previously been reported as celery volatiles. Unusually, three constituents alone made up *ca* 70% of the total volatiles, 4,7-dimethoxy-5-(prop-2-enyl)benzo-1,3-dioxolan or apiole (*ca* 23%), 3-butylphthalide (*ca* 22%) and 3-butyltetrahydrophthalide or sedanolide (*ca* 24%). The latter two compounds are known to possess strong characteristic celery aroma. Some of the relatively uncommon celery volatiles, including three newly identified, have also been detected in parsley leaves and may, therefore, be characteristic to some extent of the Umbelliferae.

INTRODUCTION

Celery (*Apium graveolens* L.) is a member of the Umbelliferae cultivated for its leaf stem which is mainly eaten raw, especially in salads, but which is also used as a cooked vegetable and in soups. The 'seeds' are also used, for flavouring purposes, and most early work on the aroma volatiles of celery was in fact carried out on the seeds. The first detailed work on the volatiles of the stem was conducted by Gold and Wilson, and reported in a series of classic papers published during the 1960's [1–6]. Possibly most interesting in this work was the identification of four unique alkylidenephthalides, claimed to be characteristic flavour components of celery [2, 3], but since then these compounds have not often been reported as celery volatiles, and in subsequent work, Wilson was unable to detect them [6]. However, amounts present would be very small, and since that time there have not been many studies on the flavour of fresh celery [7]. In this paper we report the results of analysis of the aroma volatiles of a local variety of celery grown in Libya.

RESULTS AND DISCUSSION

Fresh celery was purchased from local markets in Brack, Libya, and a valid aroma extract was prepared using well-established procedures. It was concentrated by high vacuum-low temperature distillation [8], and the resultant essence was found, on appropriate re-dilution, to possess a strong characteristic celery aroma.

The sample was analysed by GC and GC/MS, results are given in Table 1. A number of GC columns was used, but mainly fused silica capillary columns containing either bonded-phase BP1 (equivalent to OV 101) or BP20 (equivalent to PEG 20M). The retention data given in Table 1 were obtained using a 25 m fused silica column (BP1). Literature Kováts retention indices [9, 10] of most components (on OV 101) are also included in the Table, and confirm the general elution sequence. The qualitative data in Table 1 were obtained using both capillary columns; some components were more readily identified by GC/MS using one particular phase. Where positive identities are given, the mass spectra obtained on GC/MS agreed with those in the literature.

The quantitative data in Table 1 show that in total about 17.5 μg of aroma components were obtained per gram of fresh celery. This is a relatively low concentration, but Gold and Wilson found only 1 ppm total volatiles in their work [1]. Taking into account the noticeable, characteristic flavour of fresh celery, the significant aroma components must have fairly low odour thresholds. Overall, 42 components were detected as celery volatiles, of which 24 (comprising *ca* 94.4% w/w of the sample) were positively identified, with a further 3 (*ca* 0.9%) partially characterized. The 15 (*ca* 4.7%) unidentified components are not included in Table 1, and were present in the sample in such low amounts that either no mass spectrum could be recorded or the spectrum was too poor for interpretation. Of the fully identified components, 9 are reported as celery volatiles for the first time, and these are indicated in Table 1 by '+'.

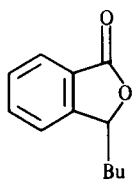
With regard to the nature of the aroma components of celery, it is interesting—and relatively unusual—to find that three constituents alone made up *ca* 70% of the total volatiles. One of these, apiole (*ca* 23%), together with the related myristicin (*ca* 2%), has been known as an important component of celery seed oil for some time, since 1955 [11]. It is noteworthy that these two compounds are also major aroma constituents of parsley, another member of the Umbelliferae [12]. However, it is perhaps a little odd that they have not previously been reported as major components of celery stem or leaf, particularly during the high-sensitivity work of Gold and Wilson [1–6].

The other two major aroma components of celery identified in this work are both alkylphthalides (strictly lactones), namely 3-butylphthalide (**1**, *ca* 22%) and 3-butyltetrahydrophthalide, or sedanolide (**2**, *ca* 24%). The latter was identified in celery as long ago as 1897 [13], and

Table 1. Volatile components of celery

Component	New	R_t (min)*	Kováts index (lit.)†	% relative abundance	μg/g
Acetaldehyde		1.5	363	1.2	0.21
Ethanol	+	1.7	500	2.2	0.39
Pentane	+	1.8	500	1.5	0.26
But-2-enal		2.0	520	0.2	0.04
Pentanal		3.4	694	0.5	0.09
Hexanal		4.8	780	2.7	0.47
Branched chain C_8 hydrocarbon		5.1		0.1	0.02
2-Pentylfuran	+	12.5	983	0.6	0.11
p-Cymene		13.9	1020	1.0	0.18
Limonene		14.4	1030	2.0	0.35
4-Isopropenyl-1-methylbenzene	+	17.3		0.7	0.12
Pentylbenzene		20.8		0.4	0.07
4-Isopropylcyclohex-2-enone (cryptone)	+	21.4		1.0	0.18
p-Mentha-1,3,8-triene	+	21.9		2.3	0.40
p-Methylacetophenone	+	22.5	1166	1.2	0.21
Carvone		24.4	1228	0.3	0.05
Carvyl acetate		34.1		0.8	0.14
β-Selinene		35.0		2.4	0.42
Valencene	+	35.2	1487	0.5	0.09
α-Selinene	+	35.3		0.3	0.05
4-Methoxy-6-(prop-2-enyl)benzo-1,3-dioxolan (myristicin)		36.1		1.9	0.33
Sesquiterpenol (M = 220)		38.9		0.5	0.09
Sesquiterpene		39.4		0.3	0.05
3-Butylphthalide		41.2		22.3	3.90
4,7-Dimethoxy-5-(prop-2-enyl)-benzo-1,3-dioxolan (apiole)		42.6		23.2	4.06
3-Butyltetrahydrophthalide (sedanolide)		44.0		24.4	4.27
3-Butyl-4,5-dihydrophthalide (sedanenolide)		44.2		0.8	0.14

*Order of elution from a BP1 GC column.
†Lit. [9, 10].



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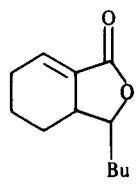

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the former was identified in celery seed oil in 1963 [14]. Wilson then detected both in the volatiles from the stem of fresh celery [6], but found less than in our present analysis, and rather different relative amounts (i.e. the ratio of 3-butylphthalide to sedanolide was about 4:1). Both compounds have been shown to possess strong, characteristic odour and flavour of fresh celery [6], so there is little doubt that the relatively high concentrations detected in this work must contribute favourably to the good flavour of the Libyan celery. On the other hand, the four alkylidenephthalides detected in minute (sub-ppm), but unspecified, amounts in celery stem volatiles by Gold and Wilson and found to have significant celery-like aroma [2, 3], could not be detected in the present work. Clearly, specific searches were made for these four compounds [3-(2-methylpropylidene)phthalide, 3-(3-methylbutylidene)phthalide, 3-(2-methylpropylidene)-3a,4-dihydrophthalide and 3-(3-methylbutylidene)-3a,4-dihydrophthalide], but none could be found. If present, amounts must have been less than the detection limits in this work (*ca* 0.01 μg/g).

Some previous workers have been unable to detect 3-butyltetrahydrophthalide together with 3-butylphthalide in celery and have suggested that the former has been confused with the latter [14, 15]. However, both were clearly, and separately, identified in this investigation (as well as by Wilson [6]), so there seems little doubt that both are, in fact, genuine celery aroma volatiles.

Another seemingly long-established phthalide volatile of celery was 3-butylidinetetrahydrophthalide (or sedanonic anhydride), first reported by Ciamician and Silber in 1897 [13], but this has since been shown to be an incorrect identification and the compound to be 3-butyl-4,5-dihydrophthalide (named sedanenolide) instead [15]. We

detected a small amount of this compound as well in our celery sample (*ca* 0.8%).

With regard to the minor celery volatiles, the results reported here agree well with the early work of Wilson [4, 6], and we too found limonene and β-selinene to be the major mono- and sesqui-terpenes, and carvone and carvyl acetate to be the major terpene carbonyl compounds.

Finally, it is interesting to note that three of the newly identified celery aroma volatiles (see Table 1), namely 4-isopropenyl-1-methylbenzene (*ca* 0.7%), 4-isopropyl-cyclohex-2-enone or cryptone (*ca* 1.0%) and *p*-mentha-1,3,8-triene (*ca* 2.3%) are also volatiles of parsley leaf, as well as the better-known apiole and myristicin [12]. Taking into account that both of these plants are members of the Umbelliferae, it is perhaps not surprising that there are some similarities between the aroma volatiles of the two species, but the above-mentioned compounds are not amongst the more common aroma volatiles, and some could therefore be considered to some extent to be characteristic of the Umbelliferae.

EXPERIMENTAL

Fresh celery was obtained from local markets in Brack, Libya.

Sample preparation. Stem and leaves of celery (360 g) were steam-distilled and the distillate extracted with CH_2Cl_2. The extract was then concd as previously described [8].

GC. FID-GC: 25 m × 0.2 mm i.d. fused silica capillary column coated with BP20 (or BP1) bonded phase; hydrogen, 1.2 ml/min; temp. programme, 70° for 5 min then 3°/min to 180°; detector and injection point heaters, 275° and 250°, respectively; injection volume, typically 0.1 μl at 25:1 split. A 5.5 m × 4 mm i.d. glass column packed with PEG 20M was also used.

GC/MS. A Kratos MS25 instrument was used, linked on-line to a Kratos DS55S data processing system. Capillary GC conditions as above were used, with He as carrier gas. The single-stage all-glass jet separator was at 250°. Significant operating parameters of the MS were: ionization voltage, 70 eV; ionization current, 100 μA; source temp., 225°; accelerating voltage, 1.33 kV; resolution, 1500; scan speed, 1 sec/decade (repetitive throughout run).

Quantitative assessment. Samples were prepared in such a manner that a known aliquot of the celery sample was analysed. Quantitative data were then derived both from the TIC monitor during GC/MS, and from the GC-FID trace during routine GC. EtOAc (0.050 M) was used as quantitative GC standard and corrections were made for the carbon-number of the identified constituents. An average correction factor was applied to unidentified GC peaks.

Acknowledgements—We thank Mr W. G. Gunn and Mr A. E. Cakebread for running the GC/MS.

REFERENCES

1. Gold, H. J. and Wilson, C. W. (1961) *Proc. Fla. St. Hort. Soc.* **74**, 291.
2. Gold, H. J. and Wilson, C. W. (1963) *J. Food Sci.* **28**, 484.
3. Gold, H. J. and Wilson, C. W. (1963) *J. Org. Chem.* **28**, 985.
4. Wilson, C. W. (1969) *J. Food Sci.* **34**, 521.
5. Wilson, C. W. (1969) *J. Food Sci.* **34**, 535.
6. Wilson, C. W. (1970) *J. Food Sci.* **35**, 766.
7. Van Straten, S., Maarse, H., de Beauveser, J. C. and Visscher, C. A. (1983) *Volatile Compounds in Foods* 5th edn. Division for Nutrition and Food Research TNO, Zeist.
8. MacLeod, A. J. and Cave, S. J. (1975) *J. Sci. Food Agric.* **26**, 351.
9. Andersen, N. H. and Falcone, M. S. (1969) *J. Chromatogr.* **44**, 52.
10. Jennings, W. G. and Shibamoto, T. (1980) *Qualitative Analysis of Flavour and Fragrance Voltatiles by Glass Capillary Gas Chromatography.* Academic Press, New York.
11. Karmajin, M. (1955) *Pharmazie* **10**, 57.
12. MacLeod, A. J., Snyder, C. H. and Subramanian, G. (1985) *Phytochemistry* **24**, 2623.
13. Ciamician, G. and Silber, P. (1897) *Ber. Dt. Chem. Ges.* **30**, 492.
14. Barton, D. H. R. and DeVries, J. X. (1963) *J. Chem. Soc.* 1916.
15. Bjeldanes, L. F. and Kim, I.-S. (1977) *J. Org. Chem.* **42**, 2333.