Phytochemistry, Vol. 31, No. 10, pp. 3621–3623, 1992
Printed in Great Britain.

0031-9422/92 $5.00+0.00
Pergamon Press Ltd

SHORT REPORTS

POLYACETYLENIC CARBONYL COMPOUNDS IN CARROTS

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(*Received in revised form* 4 *February* 1992)

Key Word Index—*Daucus carota*; Umbelliferae; carrot; polyacetylenic carbonyl compounds; falcarindiol-3-monoacetate; falcarinolone.

Abstract—Examination of the carbonyl-containing polyacetylenes in carrots showed that the previously reported compound falcarindiol-3-monoacetate consisted of a mixture of the 3-acetate and its allylic isomer, 1-acetoxyheptadeca-2,9-diene-4,6-diyn-8-ol. The other polyacetylenic carbonyl previously identified, falcarinolone, was present only as an artifact derived from autooxidation of falcarindiol during the isolation procedure.

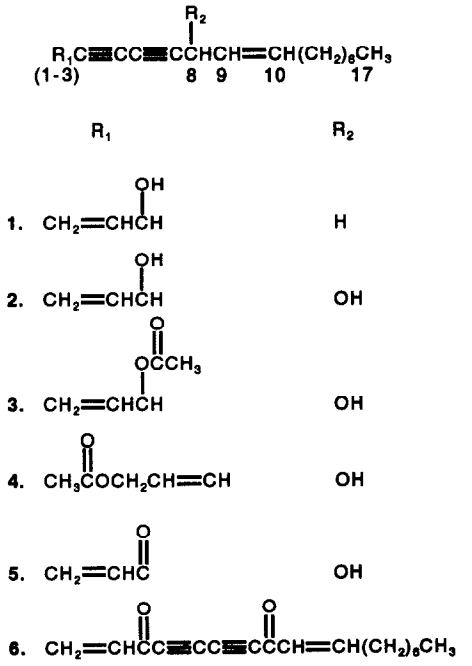
INTRODUCTION

Polyacetylenes in foods are potentially important factors in quality because they frequently exhibit toxic and antimicrobial properties. In previous studies of carrot polyacetylenes, it was also noted that most of the polyacetylenes have an unpleasant odour which may contribute to off-flavours. Bentley *et al.* [1] isolated four polyacetylenes, the alcohols, falcarinol (**1**) and falcarindiol (**2**), and two carbonyl compounds, falcarindiol-3-monoacetate (**3**) and falcarinolone (**5**) from fresh carrots. The latter compound was incompletely characterized. More recently, a number of additional polyacetylenes have been isolated from stressed carrots [2–4]. The biological significance of most of these compounds has not been determined. A review by Hansen and Boll [5] of the biological activities of compounds **1–3** and **5** as well as a number of related polyacetylenes listed some activity for all but compound **3**. Toxicity studies of the two alcohols **1** and **2** showed that only falcarinol (**1**) was appreciably toxic (LD_{50} 100 mg kg^{-1} in mice). On the other hand, antifungal activity was observed for both alcohols. In contrast, relatively little is known about the biological activities of the two carbonyl compounds, **3** and **5**.

In addition to the activity noted above, a 'rancid fat' aroma has been observed from most of the isolated polyacetylenes [4]. This property may contribute a typical off-odour to carrots containing elevated levels of polyacetylenes as a result of stress. In continuation of previous studies on the identification of carrot polyacetylenes, some of the unresolved ambiguities in the previously reported data for the two carbonyl compounds, **3** and **5** have been clarified. Further studies on the biological activities of the pure carbonyl compounds can now proceed.

RESULTS AND DISCUSSION

Re-examination of the physical data and the results of a hydrolysis reaction showed that falcarindiol-3-monoacetate (**3**) reported in several previous publications was actually the 1-acetate (**4**). This ambiguity arises because



the two acetates exist as a mixture of equilibrating isomers in which one or the other form predominates depending on conditions such as solvent polarity or concentration. In addition, the absence of falcarinolone in previous carrot samples was demonstrated by comparison with a synthetic sample made by partial oxidation of falcarindiol.

Although compound **3** has been identified in three previous carrot polyacetylene papers [2–4] (together with several similar unidentified esters), the UV spectra tended to be anomalous. The longer wavelength maxima observed [3] at 286 and 270 nm, together with maxima at 260, 246, and 232 nm are close to the UV maxima reported for **4** (2C.9C) by Bohlmann *et al.* [6]. Since the

NMR spectrum matched that previously reported for **3** (rather than **4**), there must have been a rearrangement from the 1- to the 3-isomer at some point in the NMR procedure. This was confirmed by measurement of the IR spectrum of a neat sample recovered from the NMR tube after evaporation of the deuterochloroform. The IR spectrum of this sample was identical to that of the compound designated as acetyl falcarindiol (**4**) in the initial paper [2] and unidentified compound **X** in the third paper [4]. These compounds must be the 3-acetate, since their UV data are consistent with this structure. When the neat IR sample was allowed to stand for 6 hr at room temperature, the spectrum gradually changed to that of the 1-acetate, showing that the 1- isomer is more stable under these conditions. Since part of the evidence for the identification of the 3-acetate in the second publication [3] was acetylation to the 3,8-diacetate with acetic anhydride, a rearrangement from the 1- to the 3-isomer must have taken place under the acetylation conditions.

When a sample of the 1-acetate was saponified, the crude product did not contain falcarindiol, according to IR analysis. Although the instability of this product prevented correlation with the known primary alcohol 2,9-heptadecadiene-4,6-diyn-1,8-diol expected from hydrolysis of the 1-acetyl group (ref. [6], compound **13**), it was assumed that this alcohol was the major product of the saponification. It can be concluded that the 1- isomer is the stable form under the saponification conditions.

By analogy with the well known cyclic mechanism for this type of 1,3-allylic rearrangement (a concerted pericyclic [3,3] sigmatropic rearrangement), the reaction should be stereospecific. In particular, the stereoelectronic requirements (chair-like transition state with the bulky group oriented equatorially) favour a *trans*-orientation for the 2,3- double bond in **4**. Since IR absorption bands for *trans*-double bonds at 950–960 cm^{-1} [7, 8] were not present in any of the samples containing **4**, it must be concluded that the reaction proceeds by some other stereospecific mechanism to give exclusively the isomer with the *cis*-2,3 double bond.

Compound **5** was synthesized by partial oxidation of **2** with manganese dioxide. It was accompanied by some unreacted starting material and small amounts of **6** (falcarindione). Preferential oxidation of the 3-hydroxyl group was assumed on the basis of the lower steric hindrance for oxidation of the 3-hydroxyl compared with the 8-hydroxyl. The UV and IR spectra of the two oxidation products closely resembled the spectral data previously reported for **5** and **6** [9].

Although a number of unidentified compounds showing keto and hydroxyl bands in the IR spectra were reported previously [2–4], none of the spectral data and retention properties for these compounds matched the corresponding data of authentic samples of **5** or **6**. A compound with an IR spectrum identical to that of **5** was isolated in small quantities from a sample of falcarindiol that had been prepared by preparative liquid chromatography; however, since it was not present in the original sample, it must have been an artifact produced by partial autooxidation of falcarindiol during the separation procedure.

Although a number of authors have reported the isolation of carbonyl-containing polyacetylenes related to the major carrot polyacetylene, falcarindiol, this study shows that some of these identifications may be incorrect. In the case of falcarindiol-3-monoacetate and its 1-isomer, it appears that under certain conditions these compounds may actually be mixtures of the two isomers. It is, suggested, therefore, that identification of either of these should be qualified by noting this possibility. The present study also shows that the falcarinolone previously reported as a carrot constituent is probably an artifact produced by partial autooxidation of falcarindiol.

EXPERIMENTAL

Solns were concd in a rotary evaporator at 40–50° and 40 torr. Storage and handling of concd solns was carried out in a N_2 atmosphere. Unless otherwise specified, all filtrations employed a C sintered-glass filter. *t*-Butylmethyl ether (MTBE) was HPLC grade and peroxide-free. MeCN and hexane were HPLC-grade. Et_2O was freshly distilled and peroxide-free. UV spectra were measured in Et_2O or hexane (195 nm cut-off). MnO_2 act. was assayed by a std procedure ([10], 80% yield).

Rearrangement of falcarindiol-3-monoacetate (**3**). A sample of **4** in $CDCl_3$ (as received from the NMR laboratory) was evapd (N_2) and an IR spectrum (neat) was obtained on the residue. The IR was identical with that of **3**. The neat sample (between NaCl plates) was held at room temp. for 6 hr, with periodic IR spectral analysis. The spectra gradually changed from that of pure **3** to that of pure compound **4**. No significant bands were observed in the 950–960 cm^{-1} region at any time during this period.

Hydrolysis of compound **4**. A mixt. of 5.8 mg **4** (obtained from previous studies [3, 4]), 0.15 ml MeOH, 8 mg KOH and 0.075 ml H_2O was stirred under N_2 at 50–60° for 5 min. Most of the solvent was evapd at 30°/40 torr and the product extd with 5 ml MTBE in 3 portions. The MTBE soln was extd with 4 ml H_2O (3 portions) and dried (Na_2SO_4). The product was filtered and cond (N_2) at 40°. After removal of the last traces of solvent at room temp./1 torr, the crude oily product weighed 2.7 mg (54% yield). IR ν_{max} cm^{-1}: 3740–3140 (s, OH), 2990–2870 (vs, CH), 2170, and 2070 (w, C≡C), 1750 (w), 1730 (w), 1475 (m), 1396 (w), 1373 (s), 1270 (w), 1240 (w), 1210 (s), 1090 (s), 1130 (w), 855 (m), 730 (w). Attempted purification of the crude product by TLC on reverse-phase (C18) plates [4] yielded only traces of material.

Partial oxidation of falcarindiol (**2**). A soln of 29 mg **2** in 3 ml MTBE was stirred under N_2 with 0.3 g MnO_2 for 5 min at room temp. The mixt. was filtered under pres. through a Celite pad on a fine-sintered glass funnel. The pad was washed with MTBE (60 ml). The comb. filtrates were evapd and the residual solvent removed at room temp./1 torr. The crude product weighed 16.1 mg. This was sepd on a column of Cyanopropyl Sepralyte (a surface-modified silica gel containing covalently-bonded cyanopropyl groups) packed in hexane and eluted with mixts of hexane and MTBE [3]. The mixt. contained three well-resolved peaks. The first peak eluted at 36–42 min and consisted of 0.8 mg of an oil (3% yield). The IR and UV spectral data for this compound matched those reported for **6** [9]. The second peak eluted at 100–104 min. It was an oil, weighing 6.4 mg (22% yield). The UV spectrum was the same as that reported previously for **5** [9]. The IR spectrum contained the same major absorption bands reported in ref. [9] for **5**. IR ν_{max} cm^{-1}: 3750–3100 (s, OH), 3140 (w, CH), 2940 (vs, CH), 2870 (vs, CH), 2240 (vs, C≡C), 2160 (m, C≡C), 1650 (α,β-unsatd, C=O), 1615 (C=C conjugated with C=O), 1472 (w), 1408 (m), 1394 (w), 1292 (s), 1160 (m), 1180 (w), 1135 (m), 980 (s, C=CH_2), 855 (w), 790 (m), 715 (w). The R_f for the third peak was 117–122 min. This product was an oil weighing 3.3 mg (11% yield). The R_f and IR spectrum matched that of the starting material **2**.

Isolation of **5** *from an impure sample of* **2**. A mixt. of impure frs containing **2** obtained during previous studies [3, 4] as frs from the Cyanopropyl Sepralyte column was sepd on a semiprep.

reverse-phase column (Varian MCH-10, MeCN mobile phase). A compound with an IR spectrum identical to that of **5** was isolated from a peak that eluted just after **2**. A 70 mg sample of pure **2** together with 24 mg of **5** was obtained from 159 mg of crude mixt. IR analysis showed that the original frs from which the mixt. was derived did not contain compound **5**.

Acknowledgement—NMR measurements were performed by Dr Tom Gedris at Florida State University.

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