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7-DEMETHYLPLASTOCHROMENOL-2 AND 2-DEMETHYLPLASTOQUINONE-3 FROM *SESELI FARREYNII*

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Key Word Index—*Seseli farreynii*; Umbelliferae; monoterpene; sesquiterpene quinone; demethylplastoquinone; demethylplastochromenol; artefact.

Abstract—A new chromenol, 7-demethylplastochromenol-2, a known sesquiterpene-substituted quinone, seven monoterpenes and two sesquiterpenes were isolated from the leaves of *Seseli farreynii*. Their structures were established by spectroscopic methods and chemical correlations. ©1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

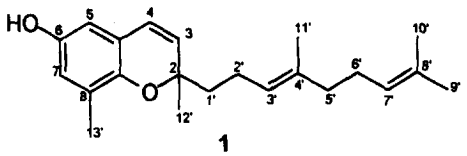
The genus *Seseli* is widely distributed in Europe and many species of this genus are rich in courmarins, some of which are known for their medicinal properties [1]. We have examined *Seseli farreynii* Molero & Pujadas, which is an endemic species of Spain, restricted to a very confined area (Creus Cape). It has been listed since April 1996 on the database of the Botanic Gardens Conservation International (BGCI) as vulnerable.

This is the first chemical investigation of this plant. We describe the structural determination of a new substituted chromenol (**1**) isolated from the ethereal extract of the leaves. The structure of the known quinone **3** is confirmed.

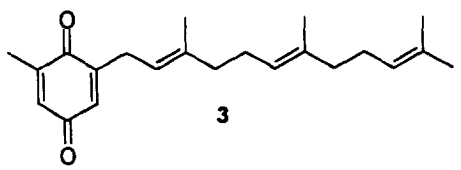
RESULTS AND DISCUSSION

GC-mass spectrometry analysis (comparison of spectra and R_i) of the crude etheral extract of fresh leaves of *S. farreynii* revealed the presence, in the order of elution, of: monoterpenes (α-pinene, 3-carene, limonene, γ-terpinene, bornyle acetate), sesquiterpenes (sabinene, terpinolene, germacrene-D, δ-cadinene), tetradecylacetate, an unknown (**1**) ($M^+ = m/z$ 326), tetracosanal, another unknown (**2**) (M^+ $m/z = 328$) (the major peak), hexacosanal and octacosanal. Furocoumarins were not present in detectable amounts.

By column chromatography, we isolated the sesquiterpene quinone **3**, previously isolated from *Ligusticum chuangxiong* [2] and identified it as 2-farnesyl-6-methyl-benzoquinone. The NMR (^1H and ^{13}C) data are in accord with the data given in ref. [2]. The same compound was earlier isolated from *S. elatum* L. (= *S. longifolium* L.), but the ring methyl was placed in the wrong position [3]. The 6 position for the methyl group can be determined in several ways by modern high resolution NMR techniques. The simplest is to observe that the two lower-field signals in ^{13}C NMR attributed to carbonyls have largely different intensities. A synomym for **3** is 2-demethylplastoquinone-3 (2-deMePQ-3). Analysis of the pure compound by GC-mass spectrometry gives mainly two chromatographic peaks, corresponding to the two unknowns **1** and **2** found on the analysis of the crude extract. It has long been known that the mass spectra of plastoquinones exhibit peaks at $[M+2]^+$ due to the formation of the corresponding hydroquinones [4]. Thus, the unknown **2** is the hydroquinone corresponding to **3**. By distillation and rechromatography of **3** we obtained **1**, whose structure is given below.



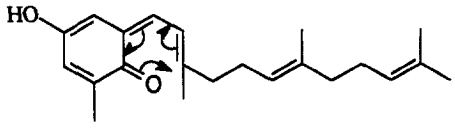
1



3

The ^1H HMR spectrum of compound **1** shows a geraniol like spectra in addition to aromatic signals. The structure shown (**1**) is in accord with the spectral values given for a chain length homologue isolated

from flue-cured tobacco leaf [5, 6]. The name proposed, for **1** in accord with these authors, is 7-demethylplastochromenol-2. The aromatic hydrogens in **1** are in the *meta* position to each other, indicated by the coupling constant (1.5 Hz). The mass-spectrum shows the loss of a methyl radical and mainly the loss of the $C_{11}H_{19}$ side chain, both giving a highly stable pyrylium ion. The previously reported mass-spectra of **3** were obtained by direct introduction. The fragmentations observed were thus the combination of the spectra of **1**, **2** and **3**. We conclude that the cyclisation of **3** occurs before ionisation, on the heated probe, and in our case in the GC injector. The probable mechanism is a thermal electrocyclic reaction of the highly favoured (all conjugated) keto-enol form (**4**) of the quinone (**3**).



4

The GC of the roots of *S. farreynii* shows **1** to be present only in trace amounts, with falcarinol dominant.

Despite the fact that **1** and **2** are artefacts, their presence is indicative of methylfarnesylquinone (**3**) which is a compound of chemotaxonomic importance being found in *S. longifolium* L. (=*S. elatum* L.), *S. gouani* Koch and *S. leucospermum* Waldst. & Kit., but not in *S. libanotis* (L.) Koch, *S. montanum* L., *S. webbii* Lowe, *S. bocconi* Guss. subsp *praecox* Gamisans, *S. peucedanoides* (Bieb.) Kos-Pol., *S. galloprovinciale* Reduron (=*S. glaucum* L.) and *S. annuum* L. (we assume that there is an error in the work of Bohlmann [3], who found the quinone in this plant. This is one more reason to add a chemical description to each known plant species).

EXPERIMENTAL

Mps: uncorr.; CC: Merck Kieselgel 60. All steps were monitored by GC-MS (HP 5890A-5970) using a 25 m BPX5 capillary (0.15 mm I.D.) GC column.

Plant material. S. farreynii was cultivated in the Conservatoire Botanique de Mulhouse (CBM), from seeds collected at the *locus classicus* of the species. Some species were collected in the wild: *S. annuum* was collected near Westhalten and near Hirzfelden (F-68), *S. libanotis* in several places in the Vosges, *S. montanum* and *S. peucedanoides* near Dijon (F-21). Others came from culture: *S. longifolium* (CBM, originating from La Clape (F-11)), *S. gouani* (Collection Pallaro—Cairate, Italy), *S. leucospermum* (Conservatoire Botanique National, Brest), *S. webbii* (CBM, from Tenerife-Canary Islands), *S. bocconi* (CBM, from Corse), *S. galloprovinciale* (CBM, from Lubéron hills (F-84), *locus classicus*). Voucher specimens are deposited at the herbarium of the Botanical Institut in Strasbourg (F-67).

Extraction and isolation. The leaves of *S. farreynii* (335 g) were extracted with Et_2O at room temp. The Et_2O extract was concd and subjected to CC on silica gel with mixts of petrol and EtOAc as eluent. The fr. eluted with a 9:1 mixt. gave 20 mg of impure **3**. Distillation in a kugelrohr apparatus (180–200°/1 mm) and rechromatography of **3** on silica gel afforded 8 mg of compound **1** (eluted with a 8:2 mixt., as a yellow oil, $C_{22}H_{30}O_2$, with no optical activity. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.36 (3H, *s*, Me-12′), 1.58 (6H, *d*, 3.6 Hz, Me-9′,10′), 1.69 (3H, *s*, Me-11′), 2.09–1.92 (4H, *m*, H-1′,2′), 2.14 (3H, *s*, Me-13′), 4.34 (1H, *s*, OH), 5.14–5.05 (2H, 2*t*, 7.8–7.8 Hz, H-3′,7′), 5.58 (1H, *d*, 9.8 Hz, H-4), 6.25 (1H, *d*, 9.8 Hz, H-3), 6.32 (1H, *d*, 2.9 Hz, H-7), 6.47 (1H, *d*, 2.9 Hz, H-5); ^{13}C NMR (69 MHz, $CDCl_3$): δ 15.52 (C-11′), 15.91 (C-13′), 17.69 (C-9′), 22.58 (C-2′), 25.71 (C-10′), 25.86 (C-6′), 26.68 (C-1′), 39.68 (C-12′), 40.76 (C-5′), 77.83 (C-2), 110.24 (C-7), 117.0 (C-4a), 121.38 (C-5), 122.82 (C-8), 124.07 (C-4), 124.32 (C-7′), 126.40 (C-3′), 130.82 (C-3), 131.37 (C-8′), 135.25 (C-4′), 144.91 (C-8a), 148.52 (C-6); MS *m/z* (rel. int.): 326 $[M]^+$ (7), 311 $[M-Me]^+$ (2), 176 (12), 175 $[M-C_{11}H_{19}]^+$ (100), 91 (2), 81 (2), 69 (4), 41 (3).

Hydroquinone **2**. MS *m/z* (rel. int.): 328 $[M]^+$ (33), 192 (22), 191 (15), 189 (10), 177 (33), 175 (32), 137 $[M-C_{14}H_{23}]^+$ (100), 109 (18), 107 (10), 95 (11), 69 (76), 41 (24).

REFERENCES

1. Nicoletti, M., Poscocco, E., Foddai, S. and Pieretti, S., *Annals of Botany*, 1990, **18**, 129.
2. Naito, T., Niitsu, K., Ikeya, Y., Okada, M. and Mitsuhashi, H., *Phytochemistry*, 1992, **31**, 1787.
3. Bohlman, F., Zdero, Ch. and Suwita, A., *Chemische Bericht*, 1975, **108**, 2821.
4. Muraca, R. E., Whittick, J. S., Doyle Daves, G., Jr, Frii, P. and Folkers, K., *Journal of the American Chemistry Society*, 1967, **89**, 1505.
5. Rowland, R. L., *Journal of the American Chemistry Society*, 1958, **80**, 6130.
6. Mayer, H., Metzger, J., Isler, O., *Helvetia Chimica Acta*, 1967, **50**, 1376.