VARIATION IN ACETYLENE CONTENT OF DIFFERENT ECOTYPES OF ARTEMISIA CAPILLARIS

KATSUMI YANO

Department of Chemistry, Fukuoka University of Education, Munakata-machi, Munakata-gun, Fukuoka 811-41, Japan

(Received 18 November 1974)

Key Word Index-Artemisia capillaris; Compositae; acetylenes; ecotypes.

Abstract—The phenylacetylenes, capillen and capillin, are the main components in both the roots and leaves of *Artemisia capillaris* growing at riverside sites, but are not present in leaves from plants growing near the sea, although found in the roots. The relationship between acetylene content and ecotype of the plant is discussed.

INTRODUCTION

In the northern region of Kyushu Island, Japan, a form of Artemisia capillaris Thunb. (Kawarayomogi) which grows near the sea at Kōnominato is different from plants growing on the banks of the River Onga. The sea-side ecotype has the following different characteristics; more crowded panicle with larger capitate flowers: thicker veined leaf with cottony hairs; longer tap and shorter lateral roots. This report discusses the differences in the acetylene content of the two ecotypes.

RESULTS AND DISCUSSION

The structures of capillen (1), capillin (2) and several other acetylenes in *Artemisia capillaris* Thunb. have been the subject of previous studies [2–8].

The extract of plants collected in June growing 3 km from the mouth of the River Onga were found to contain mainly 1 (79% in root and 88% in leaf) and 2 (20% in root and 10% in leaf), using a combination of column chromatography and preparative TLC. On the other hand, plants collected by the sea at Konominato 17 km from the river site, although containing 1 (67%) and 2 (32%) in the root, contained no isolable acetylenes

in the leaf extract. However, a very weak proton signals for the methyl group on the triple bond of 1 and 2 were found at 1.87 ppm and 2.04 ppm in the NMR spectrum of the leaf extract, showing that trace amounts of the acetylenes are present.

$$CR - C \equiv C - C \equiv C - Me$$

$$(1) R = H_2$$

$$(2) R = 0$$

The NMR spectra of the leaf extracts were measured monthly from May to September. Extracts from the roots (sea and river sites) and the leaf (river site) showed proton signals corresponding to 1 (1.87, 3.63 and 7.28 ppm) and 2 (2.04 ppm) in each case. However, in leaf extracts from plants growing by the sea-side, there were only very weak methyl signals corresponding to the acetylenes. It is obvious that the content of acetylenes in the population of A. capillaris growing at the two different sites is remarkably different, and that this may be closely related to differences in form or of environment.

EXPERIMENTAL

UV spectra were measured in EtOH. IR spectra were in CCl₄ and liquid film, NMR spectra were determined using Me₄Si as an internal standard in CDCl₃.

Extraction and separation of acetylene components. Fresh roots (1 kg) and leaves (4 kg) of A. capillaris, collected in

^{*} Natural Acetylenes, Part 2. Part 1 in [1].

1784 K YANO

June at the sea-side near Kōnominato in Fukuoka prefecture, were chopped finely and extracted with benzene (10 l. to root and 30 l. to leaf) for 2 weeks at room temp. The extract of the root was 2·7 g and the leaf 1·48 g. In the same manner, roots (2 kg) and leaves (6 kg) of river-site plants were extracted giving 4·1 g and 31·2 g respectively. Each extract was chromatographed on deactivated alumina with n-hexane, C₆H₆-EtOAc (4·1 vol. %) and EtOAc, and divided into 3 fractions. Acetylene content in the root extract of sea side plants was 18% but only a trace was found in the leaf extract. Extracts of roots and leaves of river grown plant, both contained 16% acetylenes.

Capillen (1) was isolated from the first fraction by TLC (R_f 0.65) developed with n-hexane–EtOAc (17:3 vol. %), and identified (UV, IR, NMR) by comparison with an authentic specimen [4,9].

Capillin (2) was isolated from the first and second fractions by TLC (R_2 0.53), and identified as for (1) [2].

NMR and TLC. Fresh roots and leaves were collected monthly* and extracted with C_6H_6 for 2 weeks. NMR spectra

of the extracts were measured. Extracts were also examined by TLC.

REFERENCES

- Yano, K., Takahashi, S. and Furukawa, T. Part 1 (1972) Phytochemistry 11, 2577.
- 2. Imai, K. (1956) J. Pharm. Soc. Japan 76, 405.
- Harada, R. (1956) J. Chem. Soc. Japan, Pure Chem. Sect. 77, 990.
- Harada, R. (1957) J. Chem. Soc. Japan, Pure Chem. Sect. 78, 415
- Harada, R., Noguchi, S. and Sugiyama, N. (1960) J. Chem. Soc. Japan, Pure Chem. Sect. 81, 654.
- Miyazawa, M. and Kameoka, H. (1973) The 28th Annual Meetings of the Chemical Society of Japan. Tokyo, April
- Miyazawa, M. and Kameoka, H. (1974) The 30th Annual Meetings of the Chemical Society of Japan, Higashiosaka, April 2.
- Miyazawa, M. and Kameoka, H. (1974) The 18th Symposium on Chemistry of Terpenes, Essential Oils and Aromatics, Chiba, September 28.
- Harada, R. (1957) J. Chem. Soc. Japan, Pure Chem. Sect 78, 1031.

^{*}The plants at the time of flower bud and flower were collected in the end of August and September respectively.