Phytochemistry, 1972, Vol. 11, pp. 2577 to 2579. Pergamon Press. Printed in England.

SHORT COMMUNICATION

POLYACETYLENE COMPOUNDS FROM JAPANESE MUGWORT

KATSUMI YANO, SACHIKO TAKAHASHI and TOHRU FURUKAWA

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

(*Received* 3 *March* 1972)

Key Word Index—*Artemesia princeps;* Compositae; mugwort; C_{14}-acetylenes.

Abstract—C_{14}-Polyacetylenes artemisia ketone (I) and spiroketalenolether polyyne (*cis* II and *trans* III), were isolated from the root of Japanese mugwort; *Artemisia princeps* Pamp. These components are different from those of the European plant (*Artemisia vulgaris* L.).

INTRODUCTION

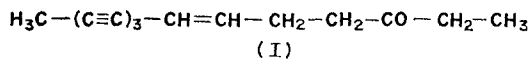
JAPANESE mugwort (Yomogi; *Artemisia princeps* Pamp.) is the most common plant of the genus *Artemisia* in Japan. The volatile constituents from the leaves of Japanese mugwort have been reported by Tsubaki *et al.*,[1] but the polyacetylene components have not so far been studied. Several investigations have been reported the polyacetylene compounds isolated from the roots of European mugworts (*Artemisia vulgaris* L.),[2–7] and this report presents an analysis of the polyacetylene constituents from the roots of mugwort collected in the Fukuoka prefecture of Kyushu Island in Japan.

RESULTS AND DISCUSSION

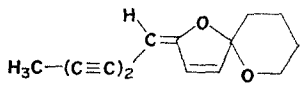
Some botanists regard Japanese mugwort as a variety of the European plant (*Artemisia vulgaris* L.). *Artemisia vulgaris* L. var. *indica* Max. was adopted by Makino[8] and *Artemisia vulgaris* L. var. *maximowiczii* Nakai by Nakai.[9] Other botanists have postulated that the Japanese mugwort is a different species from the European plant, and have given the name of *Artemisia princeps* Pamp.[10–12]

[1] N. TSUBAKI, K. NISHIMURA and Y. HIROSE, *Bull. Chem. Soc. Japan* **39,** 312 (1966).
[2] K. STAVHOLT and N. A. SÖRENSEN, *Acta Chem. Scand.* **4,** 1567 (1950).
[3] F. BOHLMANN and H.-J. MANNHARDT, *Chem. Ber.* **88,** 429 (1955).
[4] P. K. CHRISTENSEN, *Norges Tek. Vitenskapsakad.* Ser. 2, No. 7, 84 (1959).
[5] Private communication from Dr. P. HÄNEL, Organic Chemical Institute of Technical University, Berlin.
[6] This compound means not monoterpene ketone but polyacetylene ketone. F. BOHLMANN, H.-J. MANNHARDT and H.-G. VIEHE, *Chem. Ber.* **88,** 361 (1955).
[7] F. BOHLMANN, E. INHOFFEN and P. HERBST, *Chem. Ber.* **90,** 124, 1661 (1957).
[8] T. MAKINO, *Makino's New Illustrated Flora of Japan,* p. 653, Hokuryukan, Tokyo (1961).
[9] T. NAKAI, *Bot. Mag. Tokyo.* **26,** 104 (1912).
[10] R. PAMPANINI, *Nuovo Giorn. Bot. Ital.* **36,** 444 (1930).
[11] S. KITAMURA, *Memoirs of the College of Science, Kyoto Imperial University,* **15B,** 374 (1940).
[12] J. OHWI, *Flora of Japan,* Revised Edn, p. 1352, Shibundo, Tokyo (1965).

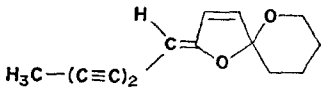
From the roots of European mugwort, dehydromatricaria ester (*cis* IV and *trans* V),[2-4] *S*-compound (VI),[5] triyne acetate (VII),[5] artemisia ketone (I)[2,6] and centaur X_3 (*trans–cis* VIII and *trans–trans* IX)[2,7] were reported. The root of Japanese mugwort, on the other hand, contains artemisia ketone (I) and spiroketalenolether polyyne (*cis* II and *trans* III)[13,14] only. Compounds I and IV–IX were isolated by Bohlmann *et al.* from roots gathered near Brauschweig in Germany,[5] while I, IV and V were found by Sörensen *et al.* from roots collected in Trondheim in Norway.[15]



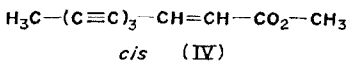
(I)



(II)

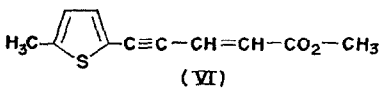


(III)

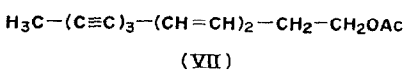


cis (IV)

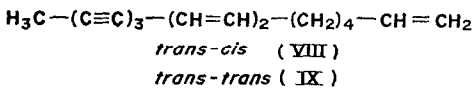
trans (V)



(VI)



(VII)



trans-cis (VIII)

trans-trans (IX)

Bohlmann and Hänel[5] examined the seasonal variation of polyacetylene compounds in the period from March till November in Germany, and did not find much change. Sörensen *et al.*[15] also found that the content of polyacetylenes varied very little in Norway over the year.

The UV spectra of the extract of Japanese root collected during May, July and September showed the absorption maxima corresponding to a mixture of I, II and III in each case.

Furthermore, these extracts gave spots corresponding only to I, II and III on TLC. So there appeared to be little variation with season. It is therefore concluded that polyacetylenes of Japanese mugwort are not identical with those of European plant (*Artemisia vulgaris* L.), and that the Japanese plant may be a different species.

EXPERIMENTAL

M.ps are uncorrected UV spectra were measured in *n*-hexane and Et_2O. IR spectra were run in $CHCl_3$ and liquid film. NMR spectrum was determined using Me_4Si as an internal standard in the CCl_4 solution.

Extraction and separation of polyacetylene components. The fresh root (30 kg) of mugwort grown at Fukuoka prefecture was collected on May, cut to small pieces extracted with Et_2O (30 l.) for 1 week at room temp. The extract (37 g, yield 0·12%) was chromatographed on alumina (Wako, 300 mesh) column. *n*-Hexane eluted hydrocarbons (52% of the extract) with no acetylene absorptivity (UV) and benzene–EtOAc (4 : 1 vol. %) eluted the polyacetylene compounds (31·5% of the extract). Finally EtOAc eluted sterols (3% of the extract).

[13] F. BOHLMANN, P. HERBST, C. ARNDT, H. SCHÖNOWSKY and H. GLEINIG, *Chem. Ber.* **94**, 3193 (1961).
[14] F. BOHLMANN, P. HERBST and I. DOHLMANN, *Chem. Ber.* **96**, 226 (1963).
[15] Private communication from Professor N. A. SÖRENSEN, The Norwegian Institute of Technology, Organic Chemistry Laboratories, Trondheim.

Artemisia ketone (I). The first fraction of the polyacetylene compounds was isolated as crystals m.p. 56·5–57·5: (lit.[6], m.p. 56·5–57·0°) recrystallized from pertoleum. R_f 0·39 on TLC with *n*-hexane–EtOAc (17 : 3). UV ($\lambda_{max}^{n\text{-hexane}}$ 232, 243·5, 258, 273, 289·5, 308, 329·5 nm, ϵ 87 200, 117 000, 4500, 7300, 11 600, 13 700, 9700) showed the existence of $(C{\equiv}C)_3$–CH=CH group, and IR (in $CHCl_3$, C≡C 2225, 2200, C=O 1715 cm^{-1} was identical with those of artemisia ketone (I).[6]

cis-*Spiroketalenolether polyyne* (II). The second fraction a resinous liquid R_f 0·38, on TLC. UV (Et_2O) 237, 250, 265, 317 nm, ϵ 8200, 3900, 3900, 14 300, showing the polyacetylene compound has a *cis*-structure.[13,14] IR (liquid film, C≡C 2230, 2135, enol ether 1625, 1580 cm^{-1}) was identical with those of authentic *cis*-spiroketalenolether polyyne (II).[16]

trans-*Spiroketalenolether polyyne* (III). From the third fraction a resinous liquid was isolated and this compound gave R_f 0·28 on TLC. UV (Et_2O) 242, 255, 310, 321 nm, ϵ 16 200, 4300, 20 000, 19 400, and showed to be *trans*-structure.[13] NMR {1·70 ppm [6H, m, $(CH_2)_3$], 1·98 ppm [3H, d, J = 1·5 Hz, H_3C–C≡], 3·90 ppm [2H, m, CH_2–O], 4·5 ppm [1H, m, HC≡C] and 6·06, 6·16 ppm [1H, d, J = 6·0 Hz, resp., HC=CH]} and IR (liquid film, C≡C 2225, 2135, enol ether 1630, 1580 cm^{-1}) were identical with those of *trans*-spiroketalenolether polyyne (III).[13]

UV and TLC. The fresh root was collected at May, July and September, and cut to small pieces. After each root was extracted with Et_2O, UV spectra were measured. The extracts were developed on TLC with benzene–EtOAc (17 : 3), and gave the spots at R_f 0·53 (correspond to II and III) and 0·62 (I). Besides, the spots at R_f 0·28 (III) and 0·39 (I and II) were chromatographed with *n*-hexane–EtOAc (17 : 3).

Acknowledgements—The authors wish to express their thanks to Professor F. Bohlmann for identification of a polyacetylene compound, to Professor N. A. Sörensen and to Dr. P. Hänel for their information on European mugwort, and to Professor E. T. Matsuura of Hiroshima University for his valuable advice through this research.

[16] Private communication from Professor F. BOHLMANN, Organic Chemical Institute of Technical University, Berlin.