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AN INSECTICIDAL DIACETYLENE FROM *ARTEMISIA MONOSPERMA*

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Key Word Index—*Artemisia monosperma*, Compositae, aromatic diacetylene, insecticide, volatile oil

Abstract—The essential oil of *Artemisia monosperma* obtained by steam distillation of the aerial parts of the plant was shown to have insecticidal activity against house fly, cotton leaf worm and the rice weevil The chemical structure of the active ingredient from the steam distillate was shown to be 3-methyl, 3-phenyl-1,4-pentadiyne

INTRODUCTION

Artemisia monosperma Delile is a herb which grows wild in the Egyptian desert under the common name 'Al-Ader' It has been shown to have several medical applications [1], and not to be attacked by insects [2]

In this communication I report that the most active insecticidal compound in the steam distillate of fresh plants of *A monosperma* is 3-methyl,3-phenyl-1,4-pentadiyne (**1**)

RESULTS AND DISCUSSION

The LD_{50}s of the solvent extracts of air dried plants, the steam distillation products of the fresh aerial parts and the column chromatographic fractions of the steam distillate from *A monosperma* were determined with house fly, cotton leaf worm and rice weevil (Table 1)

The results showed that the steam distillate was the most toxic fraction towards all the insects tested Capillary GC/MS showed that the fraction contained at least 45 volatile compounds mostly sesquiterpenes, hydrocarbons and acetylenic compounds [3–6] On CC of the steam distillate on silica gel eluted with hexane followed by ether in hexane, ether, acetone and finally methanol, most of the insecticidal activity was associated with the hexane fraction (Table 1) TLC purification of this fraction gave a single compound (99 9% by high resolution capillary GC) which was about two to four times more toxic than the column fraction and more than 10 times as toxic as the crude steam distillate

The active compound (**1**) had a molecular formula of $C_{12}H_{10}$ (*m/z* 154 0766) Its IR spectrum contained bands indicative of the presence of a monosubstituted benzene ring at 690 and 740 cm^{-1} (out of plane bending), 1500 and 1620 cm^{-1} (double bond stretching), and bands for a monosubstituted over tone from 1700 to 2000 cm^{-1} and carbon hydrogen bond stretching above 3000 cm^{-1} The presence of the monosubstituted benzene ring was confirmed by a multiplet signal in the NMR at δ7 38 (5H) The presence of the benzene ring was also evident from its characteristic ultraviolet absorbance and the formation of the ions *m/z* 77 and 51 in the mass spectrum The presence of a methyl group in the structure was based on the presence of IR absorption bands at 1390 and 1420 cm^{-1},

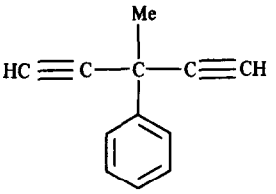

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Table 1 Insecticidal activities of the crude extracts, a column fraction and the purified acetylenic compound (**1**)

Extracts/toxicity	House fly LD_{50}*	House fly LC_{50}†	Rice weevil LC_{50}	Cotton worm LD_{50}
Hexane extract	2 01	82	104	193
Acetone extract	8 45	95	200	250
Methanol extract	9 65	120	350	400
Steam distillate	1 25	42	42	64
Hexane fraction from CC	0 31	8	12	16
TLC purified compound (**1**)	0 12	4	6	4
DDT	0 10	3	32	6
Decamethrin	0 0001			

*LD_{50} in mg/g topical applications
†LC_{50} in $\mu g/cm^2$ film applications

an NMR signal at δ1 95 (s, 3H) and the formation of the ion m/z 139 [154 − 15] in the mass spectrum Terminal triple bonds were evident from the strong IR bands at 3250 and at 2100–2300 cm^{-1}, UV absorbance at λ218 2 nm [7] and a singlet signal in the NMR at δ3 68 (2H) The above data suggested that the insecticidal compound had the structure **1** It is interesting to find such a simple hydrocarbon having relatively high insecticidal effect

Other fairly simple acetylenic hydrocarbons are known to be biologically active insecticides [8–10] Phenylheptatriyne isolated by Wat *et al* [8] is a very potent insecticide Other acetylenic compounds isolated from species in the Asteraceae have mosquito larvicidal activity [9]

EXPERIMENTAL

Plants of *A monosperma* were collected from the Western desert of Egypt during the spring of 1982 Identification of the plant was carried out by Prof N El-Hadedy, Department of Botany, Faculty of Science, University of Cairo, Egypt A reference specimen is deposited in our laboratory Plant material was washed and air dried The dried plant was then ground and extracted, first with hexane followed by Me_2CO and then MeOH On removal of the solvents under red pres 500 g of the dried plant gave 4 2 g, 5 1 g and 3 8 g of crude extracts respectively The volatile components of the plant were obtained by steam distillation of the fresh plant in a 0 7% yield

Bioassay for insecticidal activity Crude extracts and steam distillate were subjected to insecticidal activity bioassays as follows *Topical application* A susceptible strain of house fly, *Musca domistica L*, and 4th instar of cotton leaf worm larvae, *Spodoptra littorallis*, reared away from any insecticide contamination for several years were used The house flies were treated topically on the dorsum of the abdomen with 1 μl of Me_2CO containing the crude extract [11] The *Spodoptera* larvae were treated topically on the dorsal surface of the thorax with 1 μl of Me_2CO containing the crude extract The larvae were reared on castor bean leaves [12] Each group of treated flies and larvae were placed in Petri dishes and held for 24 hr at room temp then mortality percentage and LD_{50} were determined *Film applications* Different vols of the plant extracts and of the steam distillate in solns of Me_2CO were deposited on the bottom of Petri dishes The solvent was allowed to evaporate then 25 rice weevils, *Sitophilus oryzae*, were placed in each Petri dish, covered and kept at room temp for 24 and 36 hr, after which mortality and LD_{50} were calculated LD_{50} for both decamethrin and for DDT were determined under the same conditions to estimate the relative activity of the extracts and the isolated compounds

Methods TLC was carried out on silica gel (0 25 mm) developed with hexane–Et_2O–HOAc (90 10 1) Spots were detected in I_2 vapour or after spraying with anisaldehyde reagent and heating at 100° [13] Prep TLC was carried out using 1 mm silica gel plates with hexane as the solvent Spots were visualized under UV light and eluted in Et_2O

CC fractionation of the steam distillate was carried out on a silica gel column Fractions were collected using solvent systems hexane (17 fractions of 500 ml each) 1% Et_2O (12 × 200 ml), 3% Et_2O (10 × 200 ml), 5% Et_2O (10 × 200 ml) and 10% Et_2O in hexane (10 × 200 ml), Me_2CO (10 × 200 ml) and MeOH (7 × 200 ml) The fractions were freed from solvents by evaporation at red pres, weighed, analysed by TLC, GC/MS and monitored for their insecticidal activity

GC/MS was performed on a Finnigan 4530 GC/MS data system equipped with a 30 m (0 25 mm i d) WCOT-DB1 fused silica column He (40 ml/sec) was the carrier gas, the column temp started at 100° and rose to 250° at a rate of 5°/min All spectra were recorded in the EI mode at 70 eV

High resolution MS were recorded on a Du-Pont CEC 21-110 instrument (direct probe technique, 100°)

Isolation of **1** *from the steam distillate* The highest insecticidal activity was found in the column fraction which was eluted in hexane This fraction was repeatedly purified by prep TLC until the most toxic component showed one spot on TLC and one peak in the capillary GC The purified compound was obtained as a light yellow viscous liquid in 15% yield from the crude steam distillate (Found C, 93 54%, H, 6 46% Calc for $C_{12}H_{10}$ C 93 46%, H 6 54) High resolution MS m/z 154 0766 $[M]^+$, ^1H NMR (100 MHz, $CDCl_3$) δ1 95 (3H, *s*), 3 68 (2H, *s*), 7 38 (5H, *m*), EIMS 70 eV, m/z (rel int) 154 $[M]^+$ (100), 139 $[M-Me]^+$ (30), 128 $[M-C_2H_2]^+$ (16), 115 $[M-C_3H_5]^+$ (24), 77 $[C_6H_5]^+$ (25), 51 $[C_4H_4]^+$ (50) UV λ_{max}^{MeOH} nm 293 2, 278 5, 262 5, 255 2 and 218 2, IR ν_{max}^{film} cm^{-1} 3250, 2100–2300 (–C≡CH), 1620, 1500 (arom), 690, 740 (C_6H_5) and 1390, 1420 (Me), refractive index $\eta_0^{25°}$ 1 5601 The presence of terminal triple bonds was also confirmed by chemical reactions [14]

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REFERENCES

1 Fahmy, I R, Ahmed, Z F and Abdel-Moneim, F (1960) *Proc Pharm Soc Egypt* **1**, 83
2 Khafagy, S M, Metwally, A M and El-Ghazooly, M G (1979) *Egypt J Pharm Sci* **20**, 115
3 Herz, W and Santhanam, P S (1965) *J Org Chem* **30**, 4340
4 Shafizadeh, F and Bhadane, N R (1972) *J Org Chem* **37**, 274
5 Wrang, P A and Lam, J (1975) *Phytochemistry* **14**, 1027
6 Greger, H (1979) *Phytochemistry* **18**, 1319
7 Poljakov, P P (1961) in *Flora URSS* **26**, 425
8 Wat, C K, Prasad, S K, Grahm, E A, Partington, S, Arnason, T, Towers, G H N and Lam, J (1981) *Biochem Syst Ecol* **9**, 59
9 Arnason, T, Swain, T, Wat, C K, Grahm, E A, Partington, S, Towers, G H N and Lam, J (1981) *Biochem Syst Ecol* **9**, 63
10 Bohlmann, F and Kleine, K M (1962) *Chem Ber* **95**, 39
11 Saleh, M A and Casida, J E (1977) *J Agric Food Chem* **25**, 63
12 El-Defrawi, M E, El-Barawi, A A, Toppzada, A and Zeid, M (1965) *J Econ Entomol* **58**, 43
13 Stahl, E (1973) in *Drug Analysis by Chromatography and Microscopy*, p 219 Ann Arbor, Michigan
14 Schneider, F L (1964) in *Qualitative Organic Micro Analysis*, p 248 Academic Press, New York