X-ray data were collected on a Nicolet R3m diffractometer. Space group $P2_1$, $a = 12.639$ (6), $b = 7.214$ (2), $c = 15.578$ (7), A $= 110.400$ (4), $z = 2$, $\mu = (CuK_\alpha) = 5.58\ cm^{-1}$, F (000) = 520. 1931 reflections above 2.5σ (1) were used to refine to $R = 0.039$. (Additional data have been deposited at the Cambridge Crystallographic Data Centre.)

The last crystalline substance eluted with the same solvent mixture was incanilin (1), mp 184–185°, identified by comparison with an authentic sample.

Bisdehydrofruticin A (**2c**). A soln of fruticin A (**2a**) in Me_2CO was treated with Jones reagent at room temp. A slight excess was added in order to maintain an orange colour. The reaction was considered complete when a second faster moving spot had developed (TLC). The triketo compound (**2c**) was separated by prep. TLC in C_6H_6–EtOAc (4:1). **2c** showed mp 137–139°; IR ν_{max} cm^{-1}: 1700, 1710, 1730. MS m/z (rel. int.): 468 $[M]^+$, 141 (35).

Dehydrofruticin B (**3b**) was obtained by oxidation of 70 mg fruticin B, using the procedure described for the preparation of dehydrofruticin A (**2c**). Yield: 30 mg **3b**, mp 157–159°; IR ν_{max} cm^{-1}: 1710, 1730, 3450.

Bisdehydrofruticin B (**3c**). 60 mg fruticin B was obtained using the same procedure as that described for bisdehydrofruticin A. Yield: 10 mg, mp 137–140°. IR ν_{max} cm^{-1}: 1700, 1710 and 1730. MS m/z: 468 $[M]^+$.

Dihydrofruticin A (**2d**). A soln of fruticin A (100 mg) in MeOH (10 ml) was treated with $NaBH_4$ (100 mg in 10 ml MeOH). The reaction mixture was refluxed for 11 hr, H_2O added and the reduced product precipitated. The crystalline product was filtered and recrystallized from MeOH affording 85 mg dihydrofruticin A, mp 297–299°. IR ν_{max} cm^{-1}: 3400. (Found: C, 75.64; H, 10.70; O, 13.58. $C_{30}H_{50}O_4$ requires: C, 75.90; H, 10 62; O, 13.48 %.) The same substance was obtained in a similar yield by reduction of fruticin A with $LiAlH_4$.

Dehydrofruticin A (**2b**). A soln of fruticin A (130 mg) in Me_2CO was treated with Jones reagent at 0° until a yellow colour persisted. The reaction was monitored by TLC at room temp. The oxidation product (**2b**) was separated from the starting material and more advanced oxidation products by prep. TLC. Dehydrofruticin A, mp 192–194°, IR ν_{max} cm^{-1}: 1710, 1730, 3450. MS m/z (rel. int.): 470 $[M]^+$, 143 (100), 272 (87), 125 (34).

Acknowledgements—We thank MSc. José L. Villaseñor (Institute of Biology, UNAM) for identification of the plant. We are also indebted to Dr. Manuel Soriano and Quím. Rubén Alfredo Toscano for X-ray analysis and interesting suggestions.

REFERENCES

1. Polhamus, R. G. (1962) *Botany Production and Utilization. World Crops Series. Rubber*, p. 106. Interscience, New York.
2. Rodríguez, E., Yoshioka, H. and Mabry, T. (1971) *Phytochemistry* **10**, 1145.
3. Romo de Vivar, A., Guerrero, C. and Wittgreen, G. (1970) *Rev Latinoam. Quím.* **1**, 39.
4. Seidel, C. F., Felix, D., Eschenmoser, A., Bieman, K., Palluy, E. and Stoll, M. (1961) *Helv. Chim. Acta* **44**, 598.
5. Budzikiewicz, H., Djerassi, C. and Williams, D. (1964) *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol. II, p 270. Holden-Day, San Francisco.
6. Rodríguez-Hahn, L., Romo de Vivar, A., Ortega, A., Aguilar, M. and Romo, J (1970) *Rev Latinoam. Quím.* **1**, 24.

Phytochemistry, Vol 24, No 3, pp. 615–616, 1985.
Printed in Great Britain.

0031-9422/85 \$3 00 + 0.00

A FURTHER DITHIENYLACETYLENE FROM *ECLIPTA ERECTA*

P. Singh, A. K. Sharma, K. C. Joshi and F. Bohlmann*

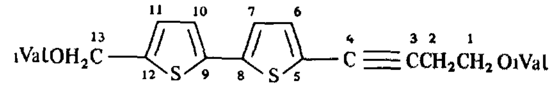
Department of Chemistry, University of Rajasthan, Jaipur, India; *Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

(*Received* 21 *June* 1984)

Key Word Index—*Eclipta erecta*; Compositae; acetylenes; dithiophene derivative.

Abstract—The roots and the aerial parts of *Eclipta erecta* afforded, in addition to compounds reported previously, a new dithienyl derivative.

Eclipta erecta L. (= *E. alba* Hassh. = *E. prostrata* L.) has been studied previously [1–3]. The roots especially are rich in thiophene acetylenes. We have re-studied a sample which was grown in the Botanical Garden of Rajasthan University. The roots gave, in addition to the compounds isolated previously [1, 2], the diisovalerate, 1. The structure followed clearly from the spectroscopic data. A broad UV maximum at 335 nm is typical for dithienylacetylenes while the ^{1}H NMR spectrum (see Experimental) indicated the presence of two isovalerate residues. A singlet at δ5.21



1

Scheme 1

(2H) and a triplet at δ4.25 (2H) further showed that these ester groups are primary. The chemical shifts agreed well with those of the corresponding diacetate which was isolated from a *Porophyllum* species [4]. The other signals also were nearly identical with those of the diacetate except those of the ester part. In addition to **1**, traces of other diesters were present which, however, could not be separated from senecioyloxymethylene terthienyl [2]. The aerial parts also gave **1** as well as the angelate of 5′-hydroxymethylene-2-(but-3-en-1-ynyl)-dithiophene [2], stigmasterol and sitosterol.

EXPERIMENTAL

The air-dried plant material (voucher deposited in RUBL Herbarium) was extracted with Et_2O–petrol (1:2) and worked-up in the usual fashion [5]. CC separation of the extract of 70 g roots gave a fraction (Et_2O–petrol, 1:4) which, by TLC (Et_2O–petrol, 1.20, several developments) finally gave, in addition of the esters reported previously [2] 3 mg 5′-isovaleryloxymethylene-2-(4-isovaleryloxy-but-3-inyl)-dithiophene (**1**), yellow oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R); UV $\lambda_{max}^{Et_2O}$ nm: 335; MS *m/z* (rel. int.). 432.142 (1.3) (calc. for $C_{23}H_{28}O_4S_2$: 432.142), 330 $[M-RCO_2H]^+$ (9), 229 $[330-RCO_2]^+$ (11), 85 $[C_4H_9CO]^+$ (80), 57 $[85-CO]^+$ (100); CIMS: 433 $[M+1]^+$ (3), 331 $[M+1-RCO_2H]^+$ (100); ^1H NMR ($CDCl_3$, 400 MHz, TMS as int. standard): 4.25 (*t*, H-1), 2.79 (*t*, H-2), 7.02 (*d*), 7.00 (*d*), 6.97 (*d*), 6.96 (*d*, H-6, H-7, H-10, H-11), 5.21 (*s*, H-13), 2.22 and 2.23 (*d*), 2.12 (*m*), 0.95 (*d*), 0.91 (*d*) (O*i*Val) [*J* (Hz): 1, 2 = 7; 6, 7 = 10, 11 = 3.5; O*i*Val: 2′, 3′ = 3′, 4′ = 3′, 5′ = 7]. The aerial parts (250 g) gave 2 mg **1**, 5 mg 5′-angeloyloxy-methylene-2-(but-3-en-1-ynyl)-dithiophene, 50 mg stigmasterol and 25 mg sitosterol. Known compounds were identified by comparing with authentic material (^1H NMR, TLC).

REFERENCES

1. Bohlmann, F., Kleine, K. M. and Arndt, C. (1964) *Chem. Ber* **97**, 2125.
2. Bohlmann, F. and Zdero, C. (1970) *Chem. Ber.* **103**, 834.
3. Bhargava, K. K. (1970) *Ind. J Chem.* **8**, 664.
4. Bohlmann, F., Jakupovic, J., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2760.
5. Bohlmann, F., Zdero, C., King, R. M and Robinson, H. (1984) *Phytochemistry* **23**, 1979.

Phytochemistry, Vol 24, No. 3, pp 616–618, 1985
Printed in Great Britain

0031-9422/85 $3.00 + 0.00

CO-OCCURRENCE OF Δ^5- AND Δ^7-STEROLS IN THE FUNGUS *DICTYUCHUS MONOSPORUS**

LINDA R. BERG, GLENN W. PATTERSON and WILLIAM R. LUSBY†

Department of Botany, University of Maryland, College Park, MD 20742, U.S.A.; †Insect Physiology Laboratory, Beltsville Agricultural Research Center, Beltsville, MD 20705, U.S.A.

(*Received* 15 *March* 1984)

Key Word Index—*Dictyuchus monosporus*; Saprolegniaceae; Oomycetes; fungi; sterols.

Abstract—The desmethyl sterol composition of the oomycete *Dictyuchus monosporus* is unusual in that it is a mixture of 56.9 % Δ^5-sterols and 42.6 % Δ^7-sterols. The Δ^5-sterols are cholesterol, 24 methylenecholesterol and fucosterol; the Δ^7-sterols are cholest-7-enol, ergosta-7,24(28)-dienol and stigmasta-7,*E*-24(28)-dienol. Stigmasta-7,*E*-24(28)-dienol is identified for the first time from natural sources. In addition, traces of lanosterol are present.

INTRODUCTION

The oomycetes have long been recognized as having sterol compositions different from the more advanced fungal groups. Most fungi contain ergosterol [1–3] but the oomycetes have Δ^5-sterols [4, 5] similar to certain algal groups [6, 7]. More recently, some of the oomycetes have been reported to contain sterols of the ergostane series instead of, or in addition to, Δ^5-sterols [8, 9]. To date, no oomycete has been found to contain both Δ^5- and Δ^7-sterols.

The co-occurrence of significant amounts of both Δ^5- and Δ^7-sterols in other organisms is uncommon. It is well-

---

*Scientific Article No. A-3793, contribution No. 6770 of the Maryland Agricultural Experiment Station.