2 Calvin, M (1983) *Science*, **219**, 24
3 Hall, D O (1985), in *Plants for Arid Lands*, (Wickens, G E, Goodin, J R and Field, D V, eds), pp 369–384 George Allen & Unwin, London
4 Szmant, H H (1986) *Industrial Utilization of Renewable Resources* Technomic, Lancaster, Pennsylvania
5 Carr, M E (1985) *Econ Botany* **39**, 336
6 Bartulin, J, Gnecco, S, Marticorena, C, Ramirez, A and Becerra, J (1984) *Bol Soc Chil Quim* **29**, 239
7 Gnecco, S, Bartulin, J, Marticorena, C and Ramírez, A (1988) *Biomass* **15** (in press)
8 Eglinton, G, González, A G, Hamilton, R J and Raphael, R A (1962) *Phytochemistry*, **1**, 89
9 Herbin, G A and Robins, P A (1968) *Phytochemistry* **7**, 257
10 Yaghmai, M S and Benson, G G (1979) *J. Nat Prod* **42**, 228
11 Eglinton, G and Hamilton, R J (1967) *Science* **156**, 1322
12 Stothers, J B (1972) *^{13}C NMR Spectroscopy, Organic Chemistry* Vol 24 Academic Press, New York
13 Mc Lafferty, F W (1963) *Mass Spectrometry of Organic Ions* Academic Press, New York

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THE DIACETYLENE 11,12-DEHYDROFALCARINOL FROM *HEDERA HELIX*

FRANK GAFNER, GARY W REYNOLDS and ELOY RODRIGUEZ*

Research Laboratories for Phytochemistry and Toxicology Department of Developmental and Cell Biology University of California, Irvine Irvine, CA 92717, U S A

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Key Word Index—*Hedera helix*, Araliaceae, polyacetylenes, contact dermatitis

Abstract—A new diacetylene, 11,12-dehydrofalcarinol, was isolated from the ornamental ivy *Hedera helix* cv Hahn's self-branching Published ^{13}C NMR assignments of falcarinol and related compounds are corrected

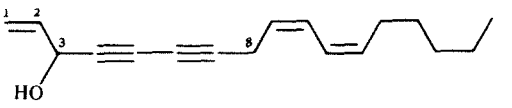
INTRODUCTION

During a recent investigation of the dermatotoxic constituents of English ivy, *Hedera helix* L (Araliaceae) [1], we isolated a new diacetylene 11,12-dehydrofalcarinol (**1**) This is a minor acetylenic constituent, present in *ca* one-tenth the amount of falcarinol (**2**)

RESULTS AND DISCUSSION

Structure was deduced from the NMR spectra in comparison with the spectra of known compounds **2** and **3** We have included the NMR spectra of our own isolations of **2** and **3**, because several of the proton and carbon assignments are incorrect in other published reports [2, 3] Assignments given in Tables 1 and 2 were unambiguously determined from COSY and HETCOR NMR spectra† The ^{1}H NMR spectrum of **2** is nearly identical to **1** except for the addition of two broad triplets at δ 6.36 and 6 15 and the disappearance of two methylene protons in the integration of resonances at δ 1 3 Both the COSY and selective proton decoupled spectra show the H-8 resonance at δ 3.17 with vicinal coupling to the δ 5 40 signal and allylic coupling to the δ 6 36 signal The same spectra show vicinal coupling between the allylic methylene resonance at δ 2.17, the δ 5 57 signal and allylic coupling with the δ 6.15 signal

The ^{13}C NMR spectrum of **1** differs from **2** with the omission of two methylene resonances at δ 29 3 and the



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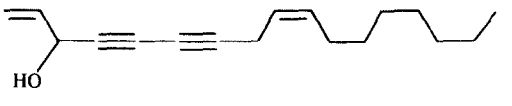

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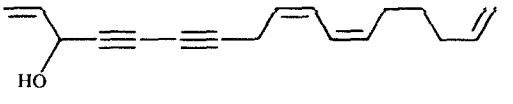

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*Author to whom correspondence should be addressed

†Copies of COSY, HETCOR and selective proton decoupled spectra of these compounds will be sent on request to the authors (ER) as supplementary material to this report

Table 1 ^{1}H NMR spectra (300 MHz, $CDCl_3$) for compounds **1–3**

H	**1** (δ)	**2** (δ)	**3** (δ)
1a	5 46 (1H, *d*, *J* = 17 1 Hz)	5.47	5.46
1b	5 24 (1H, *d*, *J* = 10 2 Hz)	5 24	5 25
2	5 93 (1H, *dd*, *J* = 17.1, 10 2, 5 4 Hz)	5 93	5 94
3	4.91 (1H, *d*, *J* = 5.4 Hz)	4.91	4 91
8	3.17 (2H, *d*, *J* = 7 2 Hz)	3.03	3 17
9	5.40 (1H, *dt*, *J* = 10 5, 7 2 Hz)	5.39	5.42
10	6 36 (1H, *ddd*, *J* = 0 6, 11 5, 10.5 Hz)	5.52	6 35
11	6.15 (1H, *ddd*, *J* = 0 6, 11 5, 10 5 Hz)	2 02	6 16
12	5 57 (1H, *dt*, *J* = 10.5, 7 8 Hz)	1 38	5 57
13	2 17 (1H, *dt*, *J* = 7 2, 7 8 Hz)	1 27	2.20
14	1.39 (1H, *quint*, *J* = 7 Hz)	1 27	1 50
15	*ca* 1 29 (2H, *m*)	1 27	2.06
16	*ca* 1 29 (2H, *m*)	1 27	5 80
17a	0 89 (3H, *t*, *J* = 6 8 Hz)	0 88	5 00
17b	—	—	4 97

Magnetic shifts of **2** and **3** are given to correct atom assignments in other reports [2, 3]. Assignments here were made from selective proton decoupled and COSY spectra

Table 2. ^{13}C NMR spectra (75.5 MHz, $CDCl_3$, int std TMS) for compounds **1–3**

C	**1** (δ)	**2** (δ)	**3** (δ)
1	117 1	116 9	116 9
2	136 2	136 2	136 2
3	63 5	63 3	63 5
4	74 5	74 5	74 5
5	71 2	71 1	71 1
6	64 4	64 3	64 4
7	79 7	80 0	79 7
8	17 9	17 7	17 9
9	122 8	122 1	123 0
10	125 9	133 0	125.8
11	122.3	27 2	122 5
12	134 8	29 3	134 2
13	27 6	29 3	27 0
14	29 2	29 3	28 6
15	31 5	31 9	33 2
16	22 5	22 7	138.4
17	14 1	14 1	117 7

Magnetic shifts of **2** and **3** are given to correct carbon assignments in other reports [2, 3] Assignments here were made from selective proton decoupling, and HETCOR spectra

addition of two vinyl carbon resonances at δ 125.9 and 122.8 which can be respectively assigned to C-10 and C-11 from the HETCOR spectrum Acetylenic carbons C-4 and C-7 were assigned by selective proton decoupling of H-3 and H-8 to suppress second order C–H coupling. Assignments for C-5 and C-6 were made by analogy with the spectrum of model compound **15** in ref. [4]

Compound **2** proved to be a potent elicitor of allergic contact dermatitis (ACD), equivalent to **1** in potential to elicit ACD on guinea pigs sensitized to the crude extract of *H. helix*. Falcarinol (**2**) was shown to be a potent sensitizer and elicitor of ACD in an experimental human sensitization [1].

EXPERIMENTAL

Hedera helix L cv Hahn's self-branching was collected in January 1987 on the campus of the University of California, Irvine. Voucher specimen no 23,181 is at the Museum of Systematic Biology of the University of California, Irvine and was authenticated by the museum botanist, Fred Roberts

Isolation Fresh stems and petioles (1 5 kg) were macerated in a blender with Me_2CO, filtered, concd *in vacuo*, and the aq remainder extracted with $CHCl_3$ The $CHCl_3$ extract was separated twice by CC over silica gel (toluene, hexane–EtOAc 19 1) to obtain 80 mg 11,12-dehydrofalcarinol (**1**), 500 mg falcarinol (**2**) and 40 mg didehydrofalcarinol (**3**) Spectral data obtained for **2** and **3** were identical to published reports [2, 3]

11,12-*dehydrofalcarinol* (**1**) Colourless oil UV λ_{max}^{hexane}: 235 nm IR ν_{max}^{neat} cm^{-1} 3350, 3075, 2940, 2910, 2810, 2240, 1635, 1455, 1410, 987, 925 CIMS (*iso*-butane, probe) 100 eV, *m/z* (rel int) 243 $[M+H]^+$ (9), 225 $[M+H-H_2O]^+$ (100), 183 (56), 169 (59), 155 (46), 141 (39), 129 (37), 117 (39)

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REFERENCES

1. Gafner, F, Epstein, W, Reynolds, G W and Rodriguez, E (1988) *Contact Derm* (in press)
2 Hansen, L and Boll, P M (1986) *Phytochemistry* **25**, 529.
3 Bruhn, G, Faasch, H, Hahn, H, Hausen, B M, Brohan, J. und Konig, W A (1987) *Z Naturforsch* **42b**, 1328.
4 Hearn, M T W (1977) *Org Magn Reson* **9**, 141