7 Kjaer, A and Thomsen, H (1962) *Acta Chem Scand* **16**, 2065

8 Kjaer, A and Thomsen, H (1963) *Acta Chem Scand* **17**, 561

9 Gaind, K. N, Gandhi, K S, Juneja, T R, Kjaer, A and Juhl Nielsen, B (1975) *Phytochemistry* **14**, 1415

10 Spinks, E A, Sones, K and Fenwick, G R (1984) *Fette Seifen Anstrichm* **86**, 228

11 Mellon, F, Chapman, J R and Pratt, J A E (1987) *J Chromatography* **394**, 209

12 Hanley, A B, Heaney, R K and Fenwick, G R (1983) *J Sci Food Agric* **31**, 863

13 Peterka, S and Fenwick, G R (1988) *Fat Sci Technol* **90**, 61

14 Cox, J, Hanley, A B, Belton, P S, and Fenwick, G R (1984) *Carbohydr Res* **132**, 323

15 Ettlinger, M G (1950) *J Am Chem Soc* **72**, 4792

16 Li Liang and Zhong Hu (1986) *J Struc Chem* **5**, 52

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N-ALKANES FROM CHILEAN EUPHORBIACEAE AND COMPOSITAE SPECIES

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Key Word Index Euphorbiaceae, Compositae, chemotaxonomy, *n*-alkanes

Abstract—The distribution pattern of *n*-alkanes in the 'refined hydrocarbon' fractions from four species of Compositae (*Lactuca serriola*, *Sonchus asper*, *Taraxacum officinale*, *Tessaria absinthioides*) and six species of Euphorbiaceae (*Adenopeltis serrata*, *Euphorbia copiapina*, *E lactiflua*, *Colliguaja dombeyana*, *C. odorifera*, *C salicifolia*) was studied Using well-established techniques, *n*-alkanes of the homologous series C_{19}-C_{33} were identified The major constituents were *n*-heptacosane (*n*-C_{27}) and *n*-nonacosane (*n*-C_{29}) Significant dominance of odd over even numbered chains and the absence of any significant quantity of branched alkanes was also found The two species of *Euphorbia* showed different distribution pattern of *n*-alkanes In two species of *Colliguaja* (*C salicifolia* and *C odorifera*), the major component was *n*-C_{27} with smaller amounts of *n*-C_{29}, but in *C dombeyana* the reverse occurred

INTRODUCTION

In recent years, there has been considerable interest in identifying and establishing new crops as renewable resources [1–5] Some of the studied plant species contain, on a dry basis, more than 5% of 'whole plant oil' (biocrude) either as the major component of a latex or distributed throughout major plant tissues

To assess the potential of the native flora, a screening programme was started and the suitability of some Chilean Euphorbiaceae and Compositae species as sources of hydrocarbon-like materials was evaluated In previous papers [6, 7] we reported that the main components of dichloromethane extracts from different plant species were *cis*-1,4-polyisoprene and waxes Analysis of the refined hydrocarbons from different species revealed almost exclusively the presence of *n*-alkanes Since *n*-alkane distributions have been utilized as taxonomic criteria [8–11], we have investigated the distribution of this type of compound in the refined hydrocarbons from the different plant species A report on the distribution of the high M_r components will be published elsewhere

RESULTS AND DISCUSSION

Refined hydrocarbons fractions, obtained from CH_2Cl_2 extracts of plant samples (leaves and stems), were analysed by IR, ^1H NMR, ^{13}C NMR, mass spectrometry and GC The results revealed the presence of *n*-alkane mixtures of chain lengths varying from *n*-nonadecane (*n*-C_{19}) to *n*-tritriacontane (*n*-C_{33}) All the spectral data obtained agreed with those reported in literature [11–13] The GC R_ts and mass spectra were compared with those of authentic standards The quantitative results are given in Table 1, they were obtained by measurement of peak areas and are expressed as a percentage of the sum of the peak areas of all compounds between n-C_{19} and n-C_{33} Our GC analysis revealed some minor peaks between those representing the n-alkanes which might be due to branched, saturated hydrocarbons. However, they occurred in amounts too small to allow reliable determination.

The most significant points emerging from the data on Table 1 are· (i) hydrocarbons were comprised of a series (C_{19}–C_{33}) of normal alkanes with odd carbon numbered chains dominant. (ii) Within the odd numbered n-alkane population of the species of the family Compositae, n-C_{29} or n-C_{27} and n-C_{29} are the dominant alkanes, representing *ca* 50 to 90% of the hydrocarbon content (iii) Within *Colliguaja* the major n-alkane is n-C_{27} with smaller amounts of n-C_{29}, except in *C. dombeyana*, in which the reverse was noted (iv) In the Euphorbiaceae either n-C_{27}, n-C_{29} or n-C_{31} was the major component In the species studied there were different distribution patterns of n-alkanes It has been previously reported that in members of this genus there are at least two distribution patterns, reflecting the fact that ***Euphorbia*** species (750) are not closely knit botanically [8]. (v) Samples of the same species collected in different places, give an almost identical distribution pattern of n-alkanes

Herbin and Robin [9] have shown, in a study of leaf cuticular waxes from a large range of Angiosperm families that n-C_{29} and n-C_{31} are the most frequent major components among the predominant odd number constituents, and that n-C_{28} and n-C_{30} are the most frequent major even-numbered constituents. The extraction procedure used in this work to obtain the refined hydrocarbon fractions would be expected to isolate most of the n-alkanes from the cuticular wax but also those from the internal tissues

EXPERIMENTAL

All plant collection and identification were done by C M. Voucher specimens are deposited in the University of Concepcion Herbarium (CONC) CH_2Cl_2 extracts were obtained from collected material (leaves and stems) These extracts were fractionated with Me_2CO to obtain Me_2CO-sol and Me_2CO-insol frs. The frs referred to as 'refined hydrocarbons' were obtained from the Me_2CO-insol fr by refluxing with activated carbon, celite and hexane, filtering and drying, as previously reported [6, 7] The yield of each fr was determined gravimetrically after removal of solvent and is expressed as per cent dry wt (Table 1)

IR of refined hydrocarbons were recorded in NaCl disks. ^{13}CNMR were obtained at 20 MHz, ^1HNMR at 60 MHz, $CDCl_3$ was solvent and TMS was int std for both NMR MS was performed under the following conditions ionization energy, 70 eV, accelerating voltage, 3 kV, emission current, 300 μA, ion source, 200°, sample, 130° GC analyses were performed by temp prog (50–260° at 6°/min) with FID and a stainless steel column (180 cm x 3 mm i d) packed with 3% SE 30, carrier gas N_2, 30 ml/min, inj temp 260°, detector temp 275°. Identification of hydrocarbons was carried out by comparison of RR_t and MS data with those of authentic standards Quantification was by peak areas

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REFERENCES

1 Hall, D. O (1983), in *Natural Resources and Development in Arid Regions* (Campos-Lopez, E and Anderson, R J., eds), pp 165–181 Westview Press, Boulder

Table 1. n-Alkanes found in refined hydrocarbon fractions from Compositae and Euphorbiaceae species

Species	% Refined hydrocarbon*	Composition (%)†									
		C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	Others
Compositae											
L serriola	1 1	—	—	†	†	†	†	92	†	3	—
S asper	0 9	—	—	†	†	4	3	82	4	4	—
T absinthioides‡	1 3	†	†	9	†	32	†	56	†	†	—
T absinthioides‡	1 3	†	†	15	†	29	†	50	†	†	—
T officinale	0 9	8	†	5	†	22	†	31	†	10	$C_{21} = 22$
Euphorbiaceae											
A serrata	0 6	†	†	8	†	8	2	74	†	2	—
E copiapina	1 1	†	†	3	†	4	†	13	3	37	$C_{32} = 25$ $C_{33} = 12$
E lactiflua	2 1	2	1	6	†	26	†	4	1	—	$C_{19} = 22$ $C_{20} = 20$ $C_{21} = 11$
C dombeyana	0 8	—	—	†	†	17	†	82	—	—	—
C odorifera‡	1 4	—	—	†	†	58	†	41	†	—	—
C odorifera‡	1 3	—	—	†	†	77	†	22	†	—	—
C salicifolia‡	1 2	—	—	†	—	98	—	†	—	—	—
C salicifolia‡	1 3	—	—	†	—	98	—	†	—	—	—

*On a dry wt basis

†Expressed as percentage of sum of peak areas of all compounds between n-C_{19} and n-C_{33}; compounds detected in percentages less than 1% are indicated by †

‡Samples collected in different places

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*

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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

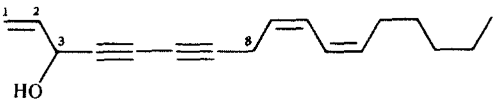
INTRODUCTION

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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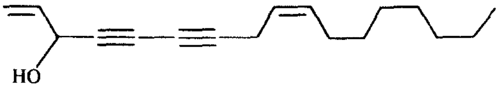

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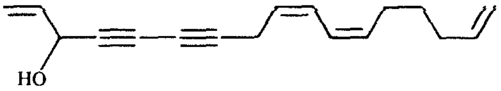

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†Copies of COSY, HETCOR and selective proton decoupled spectra of these compounds will be sent on request to the authors (ER) as supplementary material to this report