filtered and the solvent removed After prep TLC purification it yielded a compound (43 mg), mp 174–176° (from EtOAc–*n*-hexane), $[\alpha]_D^{19}$ + 52 0°(MeOH, *c* 0 74), which was identical with natural peregrinine (**1**) [lit [3] mp 172–173°, $[\alpha]_D$ + 48° (MeOH, *c* 1 0)] This identity was also confirmed by mmp, TLC and spectroscopic (IR, ^{1}H NMR, mass spectra) data

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STRUCTURE ANALYSIS OF RIMUENE BY ^{13}C NMR SPECTROSCOPY*

INNO SALASOO

School of Chemistry, The University of New South Wales, Kensington 2033, Australia

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Key Word Index—*Richea continentis*, Epacridaceae, diterpenoids, rimuene, ^{13}C NMR spectra

Abstract—A diterpenoid forming the major component of the hydrocarbon fraction of the epicuticular wax of *Richea continentis* from Baw Baw Alpine Reserve is shown to be rimuene

INTRODUCTION

In a survey of alkane distribution in the leaf epicuticular wax of Epacridaceae [1], a strong unexpected peak was observed on the gas chromatogram of the hydrocarbon fraction of the wax of *Richea continentis* B L Burtt from the Baw Baw Alpine Reserve (but not in similar material from the Kosciusko National Park) It formed 41–43% of the hydrocarbon fraction, while the major alkane, hentriacontane, was present to the extent of 21–25% The present structure analysis shows this component to be rimuene (**1**), first isolated from *Dacrydium cupressinum* Lamb (Podocarpaceae) [2] and later found in a number of other gymnosperms However, there is only one report of rimuene having been found in a dicotyledon (*Cinnamomum cassia*, Lauraceae [3])

RESULTS AND DISCUSSION

Combined GC/MS of the hydrocarbon fraction gave a very simple mass spectrum for the unknown 272 (20), 257 (100), 80 (70), which according to mass spectra catalogues [4, 5] is characteristic of rimuene However, it is known in terpene chemistry that identical mass spectra may sometimes be obtained from different compounds, e g the triterpenes of the ursane and oleanane series Therefore it was considered necessary to isolate the compound and to verify its identity by the ^{13}C NMR spectrum

The ^{13}C NMR shifts and multiplicities for olefinic carbons in the hydrocarbon were identical with those reported [6] for rimuene (**1**) [δ 111 6 (CH_2), 116 0 (CH), 145 6 (C), 146 6 (CH)] Because of the unavailability of the ^{13}C NMR shifts for the saturated carbons of rimuene, the identification of the unknown was achieved by a comparison of the ^{13}C NMR shifts of the unknown with those reported [7] for *ent*-5,15-rosadiene (**2**) (Table 1) The diene **2** differs from rimuene in having an enantiomeric nucleus and an inverted relative configuration at C-13, displaying the equatorial vinyl group Thus the ^{13}C NMR

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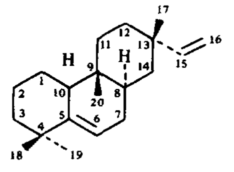

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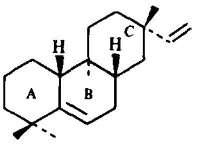

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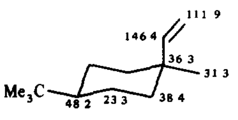

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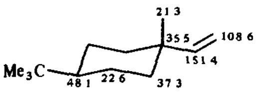

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Table 1 ^{13}C NMR chemical shifts (in ppm from TMS)

	Rimuene (this work)	Rimuene [6]	*ent*-5,15-Rosadiene [7]
C-1	26 5		26 5
C-2	21 9		21 9
C-3	40 8		40 8
C-4	35 8		36 3*
C-5	145 8	145 6	145 7
C-6	116 2	116 0	116 2
C-7	30 2		30 2
C-8	36 7		36 1
C-9	34 5		34 7
C-10	47 3		47 3
C-11	35 0		34 3
C-12	33 5		32 4
C-13	36 9		35 8*
C-14	40 3		39 1
C-15	146 8	146 6	151 3
C-16	111 6	111 6	108 4
C-17	31 6		22 4
C-18	29 4		29 3
C-19	29 7		29 7
C-20	12 6		12 4

*These values should be interchanged—see text

shifts for rimuene and the diene **2** were expected to be very similar, differing only in the ring C region Such differences in turn were expected to mimic those seen between the analogous olefins **3** (cf rimuene) and **4** (cf *ent*-5,15-rosadiene) [6]

The assignment of the ^{13}C NMR shifts of the unknown to the structure of rimuene, through the use of the shifts for the diene **2**, was straightforward in the rings A/B region In ring C the reversal of the relative configuration at C-13 led to deshielding of the now equatorial C-17 (9 2 ppm), slight deshielding (*ca* 0 7 ppm) at C-8 and C-11, and further deshielding (*ca* 1 1 ppm) at C-12 and C-14 in accord with the differences seen between the isomers **3** and **4**

Interestingly, the high-field quaternary shifts for the hydrocarbon (34 5, 35 8, 36 9 ppm) are in complete accord for those of the diene **2** (34 7, 35 8, 36 3 ppm) if the resonances reported [7] for C-4 and C-13 are interchanged, the inversion of stereochemistry having the greatest influence at C-13 (0 6 ppm) (cf 0 8 ppm in **3**, **4**)

Thus the hydrocarbon was clearly established as having the relative stereochemistry of rimuene, the absolute configuration following from its optical rotation

EXPERIMENTAL

Plant material was collected by the author Voucher specimens are kept in the Melbourne Botanic Gardens (MEL 501192) and in the Smithsonian Institute, Washington, DC (USNH 2876835)

Immersion of fresh plant material in boiling petrol [1], fractionation of the wax on neutral alumina, precipitation of alkanes from the first fraction by EtOH, and prep TLC of the residual oil on silica gel in C_6H_6 produced rimuene as the fastest-moving band, mp 46–52° (lit [2] 55 5°), $[\alpha]_D^{20}$ +51 3° ($CHCl_3$) (lit [2] +53 7°) MS *m/z* (rel int) 272 $[M]^+$ (20), 257 (100), 80 (70) (Found C, 88 2, H, 11 6 Calc for $C_{20}H_{32}$ C, 88 2, H, 11 8 %) The ^{13}C NMR spectrum (Table 1) was determined at room temp in $CDCl_3$ soln at 75 MHz

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