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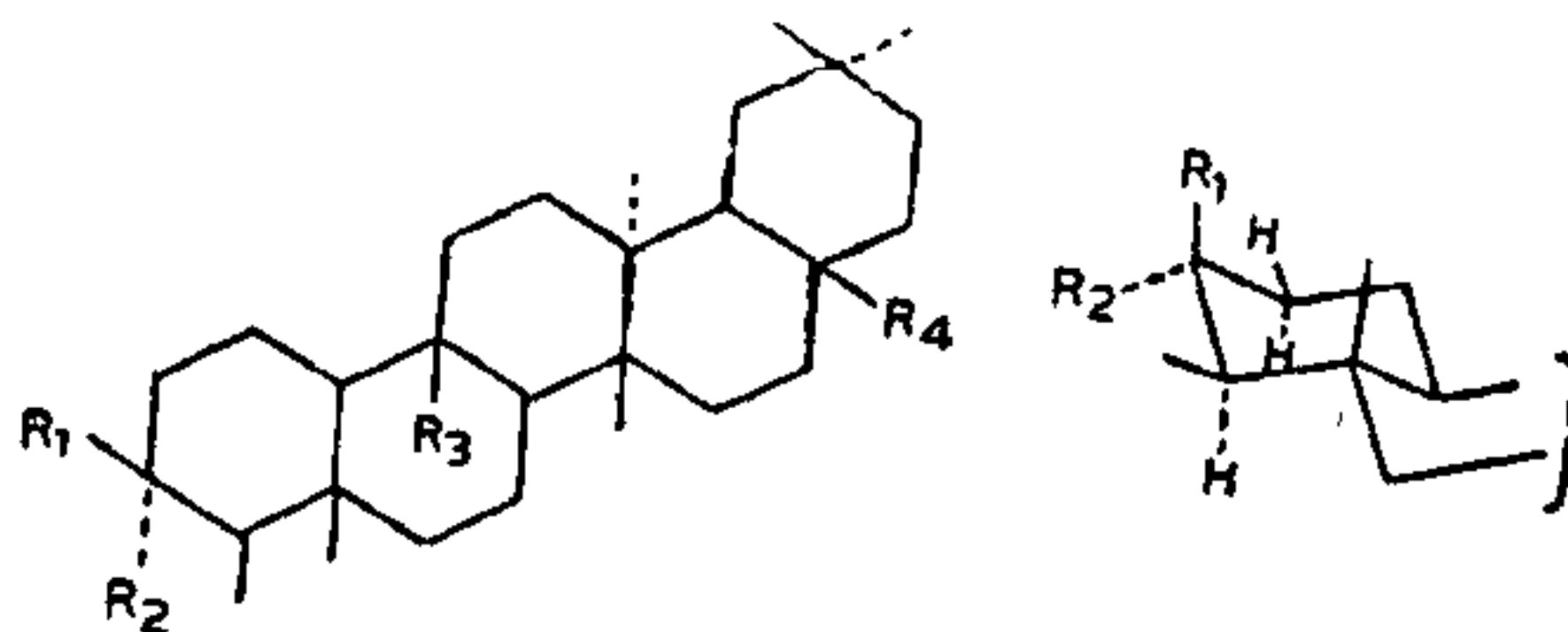
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CHARACTERISATION OF THE EPIMERIC 3 α - AND 3 β - FRIEDELAN-28- AND 25-DIOLS

REDUCTION of the 3-keto group in friedelin has been reported to give a mixture of friedelan-3 α - and 3 β -ols by several reagents^{1,2}. In our recent paper we reported the isolation of a number of 3-keto friedelane derivatives from the bark of *Elaeodendron glaucum*³. In the characterisation of friedelan-3-on-28-al (canophyllal) (I)⁴ and friedelan-3-on-25-ol (IV)², the corresponding 3 α - and 3 β - alcohols have been prepared as new derivatives by reduction of the 3-keto group with sodium borohydride and characterisation of these 3-epimeric alcohols by a study of their PMR spectra is presented now.

Canophyllal (I) on reduction with NaBH₄ in dioxan : methanol (1 : 1) solution yielded two epimeric alcohols, diol I, m.p. 248–50°; $[\alpha]_D + 20.2^\circ$, $R_f = 0.46$ (benzene), $\nu_{\text{max}}^{\text{nujol}}$: 3,495 cm⁻¹ and diol II⁵, m.p. 286–88°, $[\alpha]_D + 14.8^\circ$, $R_f = 0.18$ (benzene), $\nu_{\text{max}}^{\text{nujol}}$: 3,490 cm⁻¹ in an yield of 55% and 25% respectively. The proton α - to the 3-hydroxyl in friedelane series appears as a multiplet, the $W_{1/2}$ value of which has been used to decide the stereochemistry at this position^{5,6}. The smaller $W_{1/2}$ value (8 Hz) noticed for the multiplet 3-H signal centred at δ 3.70 in diol I suggests equatorial-axial and equatorial-equatorial couplings indicating it to be friedelan-3 β (a), 28-diol (II) with 3 α -equatorial hydrogen. The diol II with larger $W_{1/2}$ value (16 Hz) observed for its 3-hydrogen at δ 3.55 is therefore friedelan-3 α (e), 28-diol (III) with 3 β -axial hydrogen having axial-axial and axial-equatorial couplings. Govindachari *et al.*⁴, reported only one diol by reduction of canophyllol with NaBH₄

and the physical characteristics of this agreed with diol I mentioned above.



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| I | $R_1, R_2 = 0; R_3 = \text{CH}_3; R_4 = \text{CHO}$ |
| II | $R_1 = \text{OH}; R_2 = \text{H}; R_3 = \text{CH}_3; R_4 = \text{CH}_2\text{OH}$ |
| III | $R_1 = \text{H}; R_2 = \text{OH}; R_3 = \text{CH}_3; R_4 = \text{CH}_2\text{OH}$ |
| IV | $R_1, R_2 = 0; R_3 = \text{CH}_2\text{OH}; R_4 = \text{CH}_3$ |
| V | $R_1 = \text{OH}; R_2 = \text{H}; R_3 = \text{CH}_2\text{OH}; R_4 = \text{CH}_3$ |
| VI | $R_1 = \text{H}; R_2 = \text{OH}; R_3 = \text{CH}_2\text{OH}; R_4 = \text{CH}_3$ |

Similarly, friedelan-3-on-25-ol (IV) on reduction yielded the 3-epimeric diols, the major (56%)⁵, m.p. 271–72°, $[\alpha]_D + 24.2^\circ$, $R_f = 0.45$ (benzene-EtOAc, 9:1), $\nu_{\text{max}}^{\text{nujol}}$: 3,490 cm⁻¹ and the minor (30%)⁵, m.p. 244–46°, $[\alpha]_D + 18.5^\circ$, $R_f = 0.33$ (benzene-EtOAc, 9:1), $\nu_{\text{max}}^{\text{nujol}}$: 3,485 cm⁻¹. From the $W_{1/2}$ values of the 3-hydrogen, the major ($W_{1/2} = 6\text{Hz}$, δ 4.00) is fixed as friedelan-3 β (a), 25-diol (V) and the minor ($W_{1/2} = 12\text{Hz}$, δ 3.72) as friedelan-3 α (e), 25-diol (VI). It is also noteworthy that the 3 β (a)-hydrogen appeared slightly shielded, as could be expected, in both the diols (III) and (V) when compared with their respective epimers (II and IV).

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⁵ New diols gave satisfactory analysis.

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