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^{13}C NMR CHEMICAL SHIFT ASSIGNMENTS FOR GAMMACERANE (TETRAHYMANE)

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^{13}C NMR CHEMICAL SHIFT ASSIGNMENTS FOR GAMMACERANE (TETRAHYMANE)

by

D. A. Netzel[1] and D. E. Linn[2]

ABSTRACT

The carbon-13 NMR chemical shift values were obtained and assigned for each carbon atom of the pentacyclic triterpane gammacerane. Thirteen resonances of nearly unit intensity and one resonance of approximately two intensity units were observed which supports the proposed C_2 symmetry. The assignments were made by comparison with similar molecules and off-resonance decoupling. Relative to podocarpane C-7 and C-9 resonances of gammacerane were found to be shifted upfield instead of the expected downfield shift. These shifts are attributed to subtle conformational effects and an accentuated γ-effect due to the rigidity of the carbon skeleton.

INTRODUCTION

Structural elucidation of complex polycyclic natural products, especially alkaloids and steroids, has been studied extensively by mass spectrometry. An equally powerful technique for structure elucidation of natural products is ^{13}C NMR spectroscopy(1-5)[3]. However, little work has been done to date on the pentacyclic hydrocarbons possible because of limited amounts of material and limited solubility in suitable NMR solvents. Cummins and Robinson(6) have isolated a small amount of pentacyclic triterpane from Green River oil shale bitumen which was identified by Hills and Whitehead(7) as gammacerane ($C_{30}H_{52}$).

Gammacerane is a "biological marker"(8), found in oil shale. Its presence, therefore, supports the conclusion that the organic material in sedimentary deposits, such as shales, is of biological origin. Because gammacerane is a methyl substituted pentacyclic saturated hydrocarbon, its chemical shift assignments can be used to characterize ^{13}C spectra of other similar natural products. The gammacerane structure is shown in Fig. 1.

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[3] Underlined numbers in parentheses refer to references at the end of this report.

EXPERIMENTAL

Proton decoupled carbon-13 spectra were obtained using a Varian(9) CFT-20. $CDCl_3$ containing 1% TMS was used for the deuterium lock and as the solvent for gammacerane. The concentration was slightly below the saturation limit at room temperature. Chemical shifts were referenced to internal TMS and were reproducible to ±0.03 ppm. The off-resonance decoupling technique was used to identify the methyl, methylene, methine and quaternary carbons. Limited solubility of the material in $CDCl_3$ precluded using relaxation techniques for additional confirmation of assignments.

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of gammacerane shows thirteen resonances of nearly unit intensity and one of double intensity. The low number of resonances confirm that gammacerane has the proposed(7) C_2 symmetry. The carbon-13 chemical shift values and carbon assignments are listed in Table I. The chemical shift assignments were based on comparison with chemical shifts recorded for podocarpane(10) (Fig. 2), decalin and substituted methyldecalins(11,12) (Fig. 3a,b,c), and several pentacyclic triterpenoids(13-15) (Fig. 4a,b,c). The ^{13}C shifts for podocarpane are also listed in Table 1.

The resonance assignments for the ring carbons, C-1 through C-5, of gammacerane should be related to the resonance assignments of analogous carbon atoms of podocarpane, since little perturbation of these shifts is expected when additional rings are added or when a CH_3 group is substituted at C-8. Chemical shift differences for C-2, C-3 and C-4 given in Table I are indeed small. A small but significant long range δ-deshielding effect from C-26 is observed for C-1 and C-5.

The methyl substitution at C-8 in gammacerane should produce an upfield shift at C-6 and C-11 due either to steric polarization (non-bonding hydrogen-hydrogen interaction of the axial methyl, C-26, hydrogens with the axial hydrogens at C-6 and C-11) or more generally an undefined γ-gauche interaction. The γ-effect on the ring carbons of trans-decalin arising from methyl substitution (see Fig. 3a,b,c) range from -3.5 to -5.3 ppm. Thus, the predicted chemical shifts for C-6 and C-11 should be approximately 17 and 20 ppm, respectively.

The methylene carbons, C-6, as well as C-2, are assigned to the resonance of double intensity observed at 18.74 ppm. This assignment is consistance with the resonance assignment for C-6 in β-amyrin(13), 3β-acetoxyolean-12-en-29-oic acid methyl ester(14) and methyl moronate(15) (Fig. 4a,b,c). The observed shift value of 21.18 ppm was assigned to the methylene carbon, C-11. Off-resonance decoupling indicated that the multiplicity of the chemical shift value at 21.61 ppm was due to a methyl (C-29) and not a methylene carbon.

The off-resonance spectrum obtained for gammacerane although difficult to interpret because of small difference between signals indicated that the resonances at 33.08, 33.28 and 33.39 ppm are due to a methylene, quaternary and methyl carbon, respectively. Thus the C-7 was assigned the chemical shift value of 33.08 ppm. The assignment is in good agreement with the values assigned to C-7 in β-amyrin and 3-acetoxy-olean-12-en-29-oic acid methyl ester (Fig. 4a,b). This assignment, however, results in an upfield shift of the C-7 relative to podocarpane when a methyl carbon (C-26) is substituted at C-8. A deshielding β-effect would normally be expected from C-26. Apparently either the γ-gauche interactions of the methylene C-15 and methyl C-27 dominate to produce an upfield shift of 2.82 ppm or other subtle conformational effects due to rigidity of the carbon skeleton are operating.

The chemical shift value of 41.97 ppm was assigned to C-8, based upon the smaller signal intensity relative to the intensity of the signal at 42.19 ppm. Again, because of the small differences in shifts, difficulties were encountered in the absolute assignment by the off-resonance decoupling technique.

The downfield shift of 5.17 ppm for C-8 is the result of the α-substituent effect due to methyl substitution (C-26) at this position, the β-effect of the methylene carbon of ring D (C-15) and the β-effect of the methyl carbon, C-27.

Ring junction carbons C-9 and C-10 were assigned the values listed in Table I by analogy to similar carbons in 3β-acetoxy-olean-12-en-29-oic acid methyl ester, β-amyrin and methyl moronate. Relative to podocarpane the chemical shift for C-10 changed very little with addition of C-26 at C-8 and rings D and E as would be expected. However, C-9 is shielded by 5.95 ppm. This carbon is affected by a β-effect from C-26 which should produce a downfield shift, a shielding γ-gauche effect from C-27 and a small positive or negative γ-anti-effect from the methylene carbon C-15. For a similar structure such as the cis or trans 1,3-dimethylcyclohexane(16), however, the change in the chemical shift for C-2 is deshielding (+8.2 and +5.2 ppm, respectively, relative to methylcyclohexane).

Thus, the shielding effect observed for the syn-axial methyl C-25 and C-26 on C-9 could be related to subtle conformational effects due to the rigidity of the carbon skelton which results from the addition of rings D and E. It is generally believed that the six-member rings in the gammacerane molecule are in an all-trans chair conformation (see Fig. 1). The C_2 symmetry can still be preserved if ring, C, exist in a twist-boat conformation instead of the chair conformation as in podocarpane (see Fig. 5). This conformation could impose an angular stress on C-9 which would be sufficient to cause the observed upfield shift relative to podocarpane.

The methyl carbons C-23 and C-24 were assigned 33.39 and 21.61 ppm respectively, since these shifts correspond to the methyl shifts observed in podocarpane. Perturbations on the observed chemical shift due to C-26 and rings D and E were assumed to be small. Similarly, the carbon resonances for the methyls, C-25 and C-26, were assigned the values listed in Table I by analogy to similar carbons in 3β-acetoxy-olean-12-en-29-oic acid methyl ester, β-amyrin and methyl moronate. The methyl carbon, C-25, is deshielded relative to podocarpane with the substitution of C-26 at C-8. This downfield shift is attributed to the well-known δ-syn-axial effects of the two methyl groups.

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TABLE 1. CARBON-13 CHEMICAL SHIFTS FOR GAMMACERANE AND PODOCARPANE (10)

	^{13}C CHEMICAL SHIFT(PPM)		
Carbon Number	Gammacerane	Podocarpane	Difference
1,19	40.36	39.1	+1.26
2,20	18.74	19.0	-0.26
3,21	42.19	42.4	-0.21
4,22	33.28	33.3	-0.02
5,17	56.24	55.5	+0.74
6,16	18.74	21.8	-3.06
7,15	33.08	35.9	-2.82
8,14	41.97	36.8	+5.17
9,13	50.35	56.3	-5.95
10,18	37.38	36.9	+0.48
11,12	21.18	25.1	-3.92
23,29	33.39	33.6	-0.21
24,30	21.61	22.0	-0.39
25,28	15.95	14.3	+1.65
26,27	16.59		

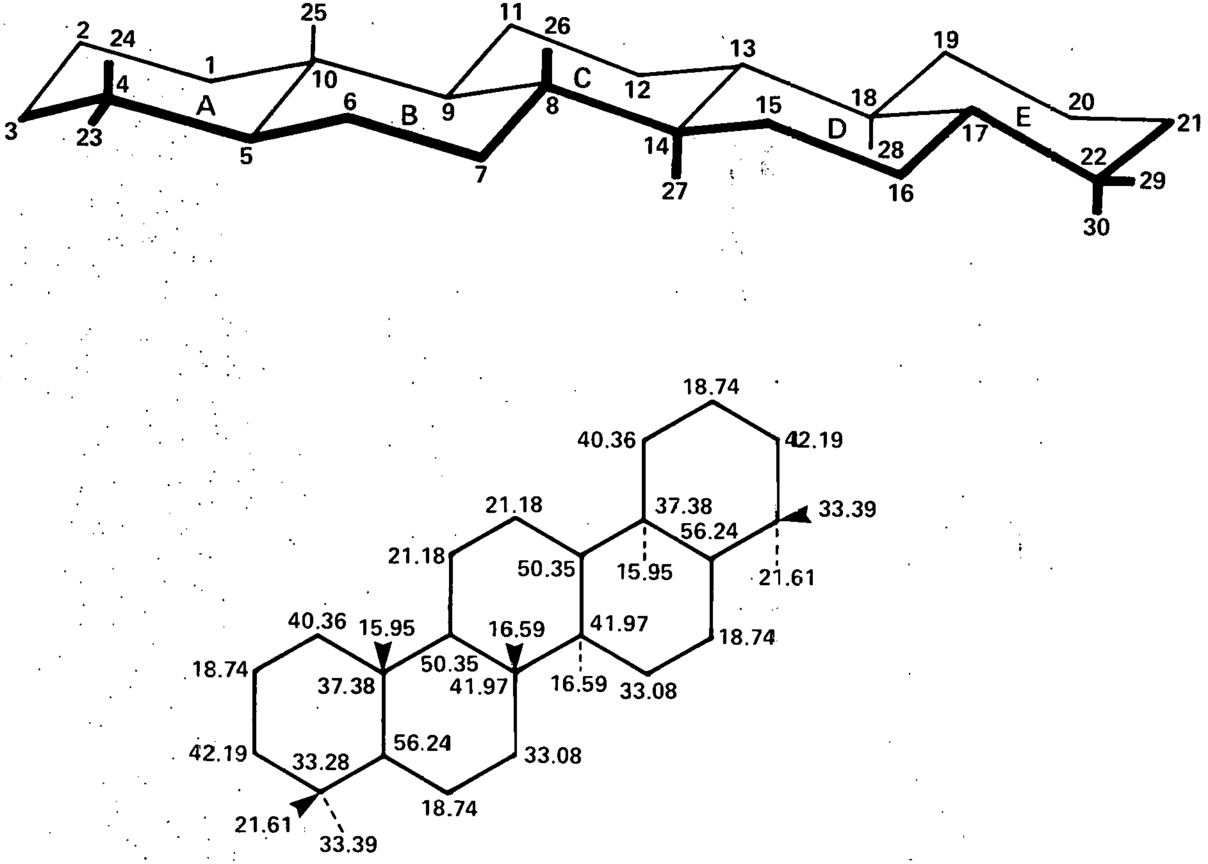

Figure 1. Numbering Scheme and ^{13}C Shifts for Gammacerane

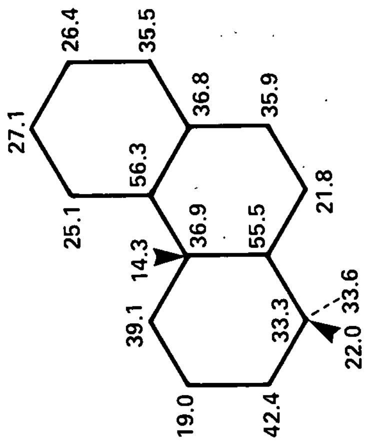

Figure 2. ^{13}C Chemical Shifts for Podocarpane (<u>10</u>)

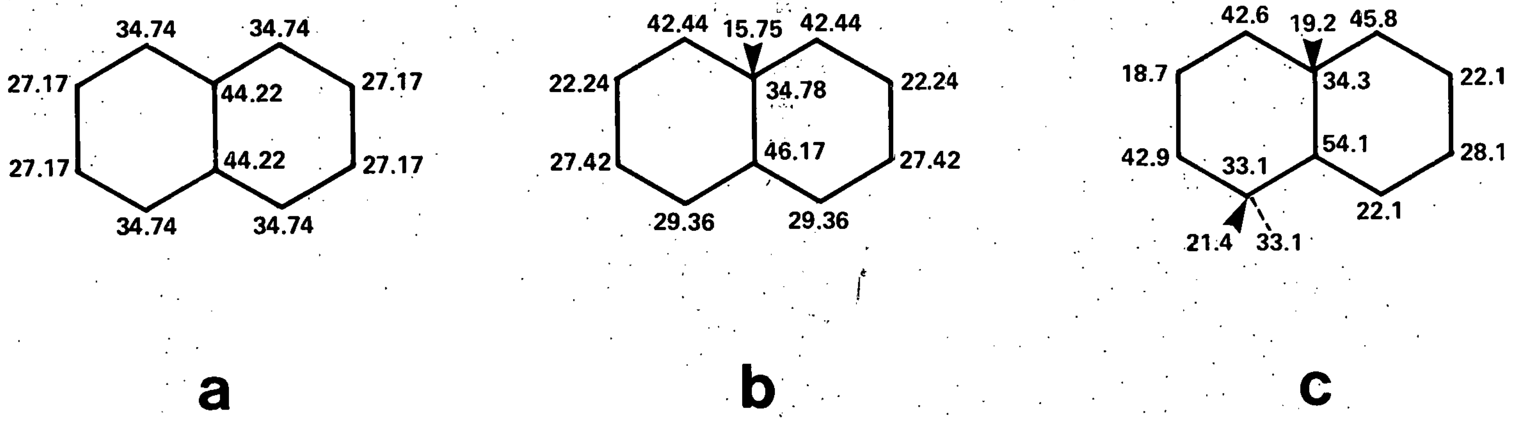

Figure 3. ^{13}Chemical Shifts for trans-decalin (11) (a), trans-9-methyldecalin (11) (b), and trans-4,4,9-trimethyldecalin (12) (c).

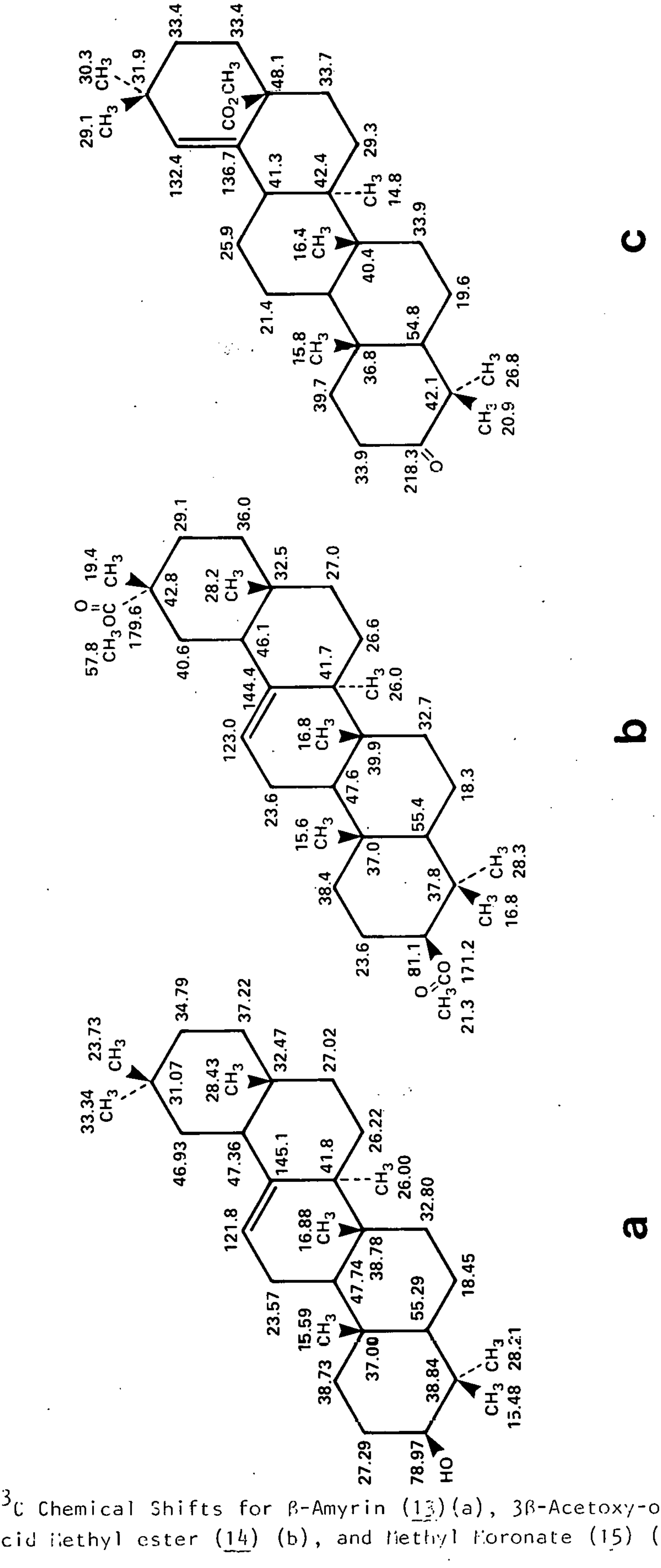

Figure 4. ^{13}C Chemical Shifts for β-Amyrin (13)(a), 3β-Acetoxy-olean-12-en-29-oic Acid Methyl ester (14) (b), and Methyl Moronate (15) (c).

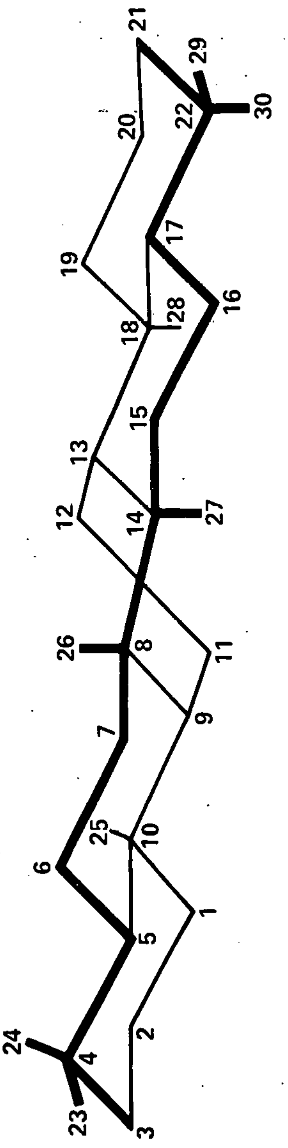

Figure 5. Twist-boat Conformation for Gammacerane