

THE STRUCTURE OF CYMBOPOGONE, A NOVEL TRITERPENOID FROM LEMONGRASS

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During investigations into the constituents of the leaf wax of lemongrass, Cymbopogon citratus Stapf, two triterpenoids were isolated, a ketone, which we have named cymbopogone, and an alcohol which has been named cymbopogonol.¹ The spectroscopic and analytical data for cymbopogone, which we present in this paper, are consistent with structure I.

Cymbopogone crystallised from ethanol as needles (overall yield based on fresh leaves 0.002%), m.p. 262-265°. The infrared spectrum indicated the presence of ketone carbonyl (1715 cm⁻¹) and carbon, hydrogen and mass spectral analysis gave a molecular formula of C₃₀H₅₀O. The mass spectrum showed distinct similarities to that of friedelin (II)² and indicated a pentacyclic triterpenoid with a D:A-friedo structure having the carbonyl group in the A-ring.³ By comparison of infrared spectra and by mixed m.p. determinations we were able to show that cymbopogone is neither friedelin (II) nor filican-3-one (III).

In the n.m.r. spectrum of cymbopogone the lowest field resonance was at δ 2.35 p.p.m.; in the methyl region only five peaks were visible: δ 0.72 (3H), 0.84 (one peak of a 3H doublet), 0.87, 0.91 and 0.96 (3H) p.p.m. In the n.m.r. spectrum of friedelin the lowest field resonance is also at δ 2.35 p.p.m., but eight peaks are clearly visible in the methyl region: δ 0.73 (3H), 0.84 (one peak of a 3H doublet), 0.87 (3H), 0.92 (one peak of a 3H doublet), 0.96 (3H), 1.01 (6H), 1.05 (3H) and 1.18 (3H) p.p.m.

In order to obtain further information about the structure of cymbopogone the n.m.r. shift reagent Eu(fod)₃ was employed. The results are given in the table along with those obtained for friedelin (II). The similarity in the induced shifts for the 4, 5, 9, 13 and

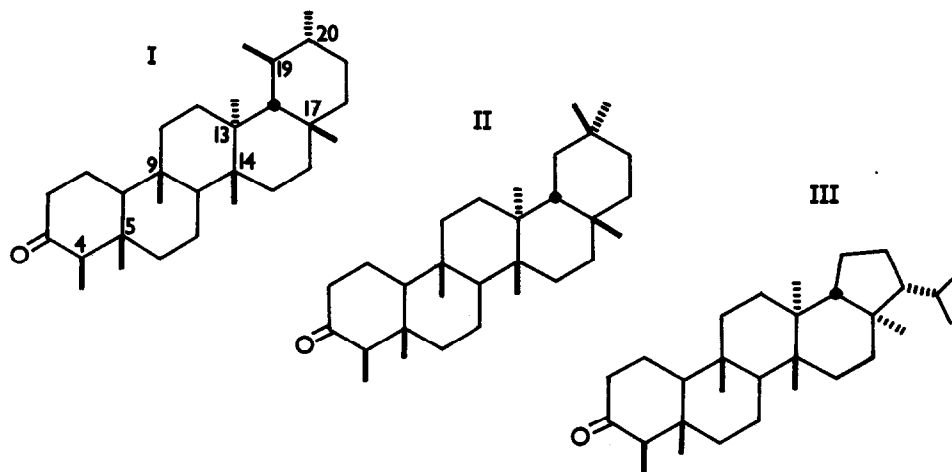


Table $\text{Eu}(\text{fod})_3$ induced shifts and chemical shifts of methyl groups^a

methyl group		4	5	9	13 ^b	14 ^b	17	other methyls	
cymbopogone	induced shift	100	65.6	19.9	10.3	12.3	4.6	4.0	3.2
	chemical shift	0.88 ^c	0.72	0.90	0.87	0.91	0.96	0.90 ^d	0.88 ^d
friedelin	induced shift	100	64.9	19.5	10.4	12.0	5.0 ^e	3.3	3.2
	chemical shift	0.88 ^c	0.73	0.87	1.01	1.05	1.18 ^e	0.96	1.01
filican-3-one	chemical shift ^f	0.88 ^c	0.72	0.92	1.00	0.92	0.82	0.84 ^e	0.89 ^e

^a. The induced shifts are relative to the 4-methyl induced shift equal to 100. The solutions of both cymbopogone and friedelin were ca. 0.03 M in CDCl_3 . The chemical shifts are δ p.p.m. Assignments for cymbopogone and friedelin are based on a comparison of the observed induced shifts with those calculated taking the O to Eu distance as 4 Å, with the O-Eu axis in the C=O plane at an angle of 140° to the axis of the C-O σ -bond and cis to C-2.⁴ ^b. For cymbopogone and friedelin the assignments for the 13 and 14-methyl groups may have to be interchanged. ^c. Doublet, $J = 6.5$ Hz. ^d. Complex multiplet. Doublet at high $\text{Eu}(\text{fod})_3$ concentrations, $J = 6$ Hz. ^e. This assignment is not definite. The resonance at δ 1.18 may be due to one of the 20-methyl groups. ^f. Unpublished data kindly supplied by Prof. H. Ageta.

14-methyl groups in cymbopogone and friedelin confirms that cymbopogone has a D:A-friedo structure. Further, it shows that the carbonyl group is in the 3-position which is in any case the most likely on biosynthetic grounds.

The chemical shifts of the methyl groups in cymbopogone and friedelin were calculated by extrapolation to zero $\text{Eu}(\text{fod})_3$ concentration. The values obtained are given in the table. The chemical shifts of the methyl groups in filican-3-one (III) are also given for comparison. The differences in the chemical shifts of both the 13 and 14 methyl groups in cymbopogone and friedelin are noteworthy but can be explained by the differences in the preferred conformations of the two compounds. In cymbopogone the D-ring takes up a chair conformation and the E-ring a boat conformation whereas in friedelin it is probable that both the D and E-rings take up boat conformations.⁵

At low concentrations of $\text{Eu}(\text{fod})_3$, i.e. with molar equivalents of $\text{Eu}(\text{fod})_3$ below 0.15, no peaks were visible for the 19 and 20-methyl groups in cymbopogone. On increasing the $\text{Eu}(\text{fod})_3$ concentration the other overlapping methyl resonances were shifted to lower field away from these methyl groups which were then seen to resonate as a broad multiplet. Only at molar equivalents of $\text{Eu}(\text{fod})_3$ over 0.5 did the 19 and 20-methyl resonances appear as overlapping doublets. This is in agreement with previous findings for the vicinal methyl groups in the ursane E-ring.^{6,7} These methyls form an AX_3Y_3 system with the 19 and 20-methine protons which results in complex resonances being produced. Since however their calculated induced shifts differ markedly, at high $\text{Eu}(\text{fod})_3$ concentrations the two methine proton resonances are shifted sufficiently apart relative to their coupling constant for the methyl resonances to be amenable to first-order analysis. It should be noted that in the n.m.r. spectra of B':A'-neogammacerane derivatives⁸ and lupane derivatives^{7,9} the isopropyl methyl groups resonate as well-defined doublets.

A compound with structure I is also highly likely on biosynthetic grounds, indeed its existence was forecast twenty years ago.¹⁰ Only three groups of pentacyclic triterpenoids have friedo-derived structures, these are: friedooleananes (D, D:C, D:B and D:A-friedo compounds are known), friedo-B':A'-neogammaceranes (D:C, D:B and D:A-friedo compounds are known) and friedoursanes (until now only D and D:C-friedo compounds were known).¹¹ Hence cymbopogone, which can be named systematically as D:A-friedours-3-one, is the missing analogue of D:A-friedoolean-3-one (friedelin) and D:A-friedo-B':A'-neogammacer-3-one (filican-3-one).

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References and Notes

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2. The mass spectrum of cymbopogone shows the following major peaks: m/e 426 (45%), 411 (6%), 383 (3%), 341 (32%), 302 (6%), 286 (9%), 273 (15%), 246 (11%), 231 (11%), 218 (17%), 205 (22%), 191 (11%), 179 (18%), 163 (15%), 149 (16%), 137 (23%), 123 (100%) and 109 (42%). The mass spectrum of friedelin shows the following major peaks: m/e 426 (29%), 411 (11%), 341 (8%), 302 (27%), 287 (12%), 273 (44%), 246 (33%), 231 (28%), 218 (37%), 205 (44%), 191 (32%), 179 (42%), 163 (48%), 149 (33%), 137 (46%), 123 (90%) and 109 (100%).
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