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REVISED STRUCTURES OF CYMBOPOGONE AND CYMBOPOGONOL

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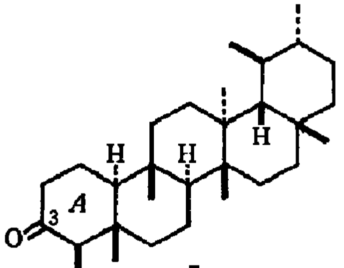
The structures of cymbopogone and cymbopogonol were revised to D:A-friedo-18β,19αH-lupan-3-one and D:A-friedo-18β,19αH-lup-4(23)-en-3β-ol, respectively.

Cymbopogone[1a)] and cymbopogonol[1)] are two triterpenes isolated from the leaf wax of lemongrass, Cymbopogon citratus Stapf. Based on spectroscopic and mass spectral data, a pentacyclic triterpene framework of a D:A-friedo type having a carbonyl group at $C_{(3)}$-position was suggested for cymbopogone. The IR spectrum and melting point showed that cymbopogone is neither friedelin (D:A-friedooleanan-3-one) nor filican-3-one (D:A-friedohopan-3-one). The ^{1}H NMR spectral investigation using $Eu(fod)_3$-d_{27} as a shift reagent together with biogenetic considerations led to a structure, D:A-friedoursan-3-one (**1**), for cymbopogone.[1a)] The structure of cymbopogonol was inferred to be D:A-friedours-4(23)-en-3β-ol (**2**) by spectral investigation and its conversion into cymbopogone.[1b)] In this communication, we wish to report revised structures, D:A-friedo-18β,19αH-lupan-3-one (**3**) and D:A-friedo-18β,19αH-lup-4(23)-en-3β-ol (**4**), for cymbopogone and cymbopogonol, respectively.

In connection with studies on backbone rearrangement of triterpene epoxides, D:A-friedo-18β,19αH-lupan-3-one (**3**) was prepared and the structure of **3** with a D:A-friedolupane skeleton was unambiguously established by X-ray crystallography of 3α,4α-epoxy-D:A-friedo-18β,19αH-lupane (**5**) derived from **3**.[2)] The ^{1}H NMR, ^{13}C NMR, IR, and mass spectra of cymbopogone were found to be completely identical with those of the synthetic triterpene ketone (**3**) (cf. Table) and no mixed melting point-depression was observed. In the mass spectrum of cymbopogone a fragment ion peak at m/z 383 due to a loss of the isopropyl group was observed, and in the ^{1}H NMR spectrum two methyls of the isopropyl group resonated at ca. δ 0.8-0.95 as complex signals overlapped with other methyl signals. A revision of the structure from **2** to **4** follows for cymbopogonol.

The occurrence of D:A-friedo-18β,19αH-lupan-3-one in nature is biogenetically reasonable, since it corresponds to an ultimate rearranged product in the migrated lupane series. Biogenesis of lupeol [lup-20(29)-en-3β-ol] has been proposed *via* pentacyclic intermediate (6) carrying a positive charge on $C_{(20)}$ or its equivalent species.[3] Deprotonation of a proton on $C_{(29)}$ could afford lupeol, while an ultimately sequential shift of methyl groups and hydrides followed by a removal of a proton on $C_{(3)}$ would give 3.



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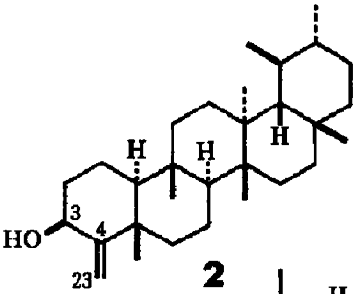

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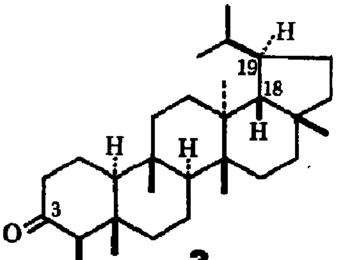

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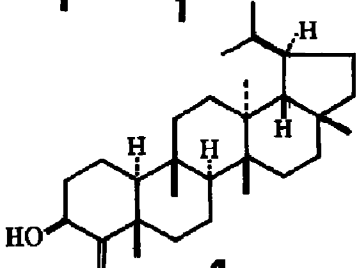

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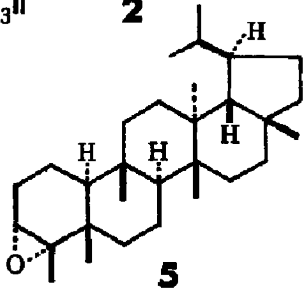

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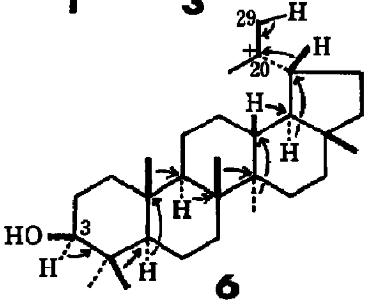

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Table Melting Points and Spectral Data for Cymbopogone and 3

	Cymbopogone	3
Mps	262-265 °C	265-268 °C (from acetone)
IR (Nujol)	1715 cm^{-1}; ref. 1a)	1715 cm^{-1}; a)
^1H-NMR	ref. 1a)	a)
Mass spectra (m/z)[b)]	426(45;M^+), 411(6), 383(3), 341(32), 123(100); ref. 1a)	426(35;M^+), 411(7), 383(3;$[M-C_3H_7]^+$), 341(29), and 123(100)
^{13}C NMR (δ_C)[c)]	6.8, 14.7, 15.8, 16.6, 18.2, 18.3, 20.9, 22.3, 23.3, 27.6, 29.3, 30.1, 32.4, 33.5, 35.0, 35.6, 37.8, 38.9, 39.1, 39.7, 41.2, 41.5, d) 43.0, 48.0, 50.9, 54.2, 58.2, 59.5, 213.1	6.8q, 14.7q, 16.0q, 16.7q, 18.2q, 18.5t, 20.8q, 22.4q, 23.3q, 27.6t, 29.6t, 30.3t, 32.6t, 33.6d, 35.2t, 35.5t, 37.9s, 39.1s, 39.2s, 39.8s, 41.4t, 41.6t, 42.0s, 43.3t, 48.2d, 51.1d, 54.4d, 58.4d, 59.7d, 212.5s

a) This is found to be identical with the corresponding spectrum of cymbopogone.
b) Numerical values in parentheses refer to relative intensities expressed in %.
c) Carbon-13 FT NMR spectra were measured with a Bruker HFX-90 and a JEOL FX-90Q spectrometer at 22.6 MHz and 22.5 MHz, respectively, using $CDCl_3$ solution. s, singlet; d, doublet; t, triplet; q, quartet. d) This signal due to a quaternary carbon was not observed under low S/N conditions.

References

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