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STRUCTURE OF SIRUTEKKONE, A DITERPENOID FROM *PREMNA HERBACEA*

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Key Word Index—*Pygmacopremna herbacea*; sirutekku; sirutekkone; diterpene; 2D NMR studies.

Abstract—The structure of sirutekkone, a constituent of *Premna herbacea*, has been established by spectral methods, especially 2D-NMR.

INTRODUCTION

The dried roots of *Premna herbacea* Roxb. (Syn. *Pygmacopremna herbacea* Moldenke), Tamil-sirutekku, are used in Indian medicine for a variety of ailments [1]. Sirutekkone was isolated from the powdered roots by solvent extraction and chromatography. Structure elucidation using spectral data revealed it to be a diterpenoid quinone methide having a novel skeleton.

RESULTS AND DISCUSSION

Sirutekkone was isolated as a yellow crystalline solid. The molecular formula was established as $C_{20}H_{24}O_4$ (*m/z* 328 and elemental analysis). It dissolved in alkali to produce an orange colour and gave an intense green colour with ferric chloride.

The UV spectrum indicated a highly conjugated chromophore. The shift of the longer wavelength absorption at 388 nm to 489 nm on addition of a drop of alkali indicated a diosphenol. The IR spectrum indicated the presence of a hydrogen bonded hydroxyl (3400 cm^{-1}), δ-lactone (1745 cm^{-1}), conjugated and hydrogen bonded carbonyl (1610 cm^{-1}) and *gem* dimethyl (twin bands at 1325 and 1315 cm^{-1}) groups.

The ^1H NMR spectrum showed a broad singlet which exchanged with D_2O (δ7.28), two olefinic doublets forming an AB quartet (δ6.52 and δ6.15, $J = 8.6$ Hz), two non-equivalent methylene protons showing geminal coupling (δ3.68 and δ2.89, $J = 15.4$ Hz), three methyl singlets (δ1.43, δ1.35 and δ1.28) and an isopropyl group (δ1.20, δ1.13, δ3.10, $J = 1.7$ Hz).

Homonuclear COSY [3] confirmed the geminal splitting of the H_a-10 and H_b-10 protons and the four line AB pattern of the two olefin protons at δ6.52 and 6.15. A $^{13}C/^1H$ heteronuclear direct correlation experiment [3] optimized for 125 Hz couplings enabled the assignment of CH_n units and the identification of quaternary carbons. Two versions of the heteronuclear remote correlation experiment were performed, both optimised for 10 Hz couplings. One employed the strategy of incorporating the evolution period in the polarization transfer period (COLOC [4]) while the other employed the same pulse sequence as for direct correlation.

Directly correlated proton shifts are given in parentheses $^{13}C(^1H)$. C-1 was assigned a shift of δ84.35 (*s*) and showed remote correlations (rc) with H-20, H-10 and H-6. C-2 and C-3 were assigned shifts of δ170.08 (*s*) and 42.63 (*t*) (2.52, 2.56) respectively; C-2 showed a rc with H-3. C-4 was assigned the shift of δ37.68 (*s*) and had rcs with H-18 and H-19. The carbon shifts δ117.09 (*d*) (6.15), 137.92 (*d*) (6.52), 137.79 (*d*) (6.80) were assigned to carbons 6,7 and 14 respectively. H-6 and H-7 gave rise to an AB quartet, C-6 and C-14 showed rc with H-7 and C-7 showed a rc with H-14 confirming the assignment. C-5, C-8 and C-9 were assigned the shifts of δ134.10 (*s*), 113.95 (*s*), 147.58 (*s*) respectively. While they all showed rcs with H-10, C-5 showed a rc with H-6 and C-8 showed a rc with H-14. C-10 could be unambiguously assigned the shift of δ38.76 (*t*) (3.68, 2.89). H-10 rcs were seen for C-1, C-5, C-8 and C-9 as would be expected. C-11 carrying the OH was assigned the low field shift of δ159.39 (*s*) and it showed a rc with H-10. The lowest field shift of δ179.15 (*s*) was assigned to the ketone C-12 and it showed a rc with H-14. The signals at δ142.09 (*s*) and 26.95 (*d*) (3.10) which showed rcs with the isopropyl methyl protons were assigned to C-13 and C-15 respectively. While the angular methyl group whose protons showed a rc with C-1 could be identified, the *gem* dimethyls and isopropyl methyls could not be individually assigned by these experiments owing to insufficient digital resolution in the F_1 dimension. If structure **2** was to be applicable, the shift of δ84.35 would have to be assigned to C-4 and in this assignment its rcs with H-20 and H-10 could not be accounted for.

EXPERIMENTAL

Mp: uncorr; NMR studies were performed in TMS–$CDCl_3$ on a Bruker CXP-90 FT NMR spectrometer at ambient temperatures, 28 ± 1°. ^1H decoupler and ^{13}C 90° pulse widths were respectively 38 μsec and 10 μsec. The heteronuclear 2D NMR data were acquired as a 65 × 1024 matrix, zero filled to 256

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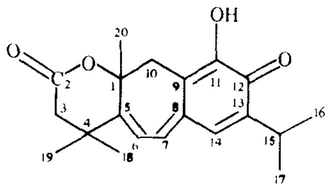

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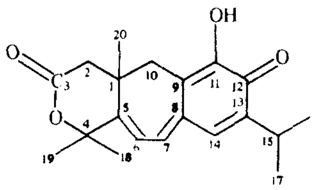

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Fig. 1. Carbon numbering is based on that in andromedane [2].

Table 1. ^{13}C NMR and ^{13}C/^{1}H 2D NMR data (22.64/90.02 MHz, $CDCl_3$, TMS as internal standard)

C	^{13}C SFORD	^{13}C/^{1}H Direct correlation	^{13}C/^{1}H Remote correlation COLOC	^{13}C/^{1}H Remote correlation
1	84.35 (*s*)		6.15, 1.43	6.15, 3.68, 2.89, 1.43
2	170.08 (*s*)		2.52	2.52
3	42.63 (*t*)	2.52, 2.56	2.52	2.52
4	37.68 (*s*)		1.28	1.28, 1.35
5	134.10 (*s*)		3.68	3.68, 6.15
6	117.09 (*d*)	6.15		6.52
7	137.92 (*d*)	6.52		6.52, 6.80
8	113.95 (*s*)		3.68, 6.80	3.68, 2.89
9	147.58 (*s*)		3.68, 2.89	3.68, 2.89
10	38.76 (*t*)	3.68, 2.89	3.68, 2.89	3.68, 2.89
11	159.39 (*s*)		1.35	3.68, 1.35
12	179.15 (*s*)		6.80	6.80
13	142.09 (*s*)		1.20	1.13, 1.20
14	137.79 (*d*)	6.80	6.80	6.80, 6.52
15	26.95 (*d*)	3.10	1.20	1.13, 1.20
16	21.70 (*q*)	1.20	1.20	1.20, 1.13*
17	21.61 (*q*)	1.13	1.20	1.13, 1.20*
18	29.65 (*q*)	1.28	1.28	1.35†
19	28.47 (*q*)	1.35	1.35	1.35, 1.28†
20	23.71 (*q*)	1.43	1.43	1.43

*16 and 17 may be reversed.
†18 and 19 may be reversed.

× 1024, yielding a 256 × 512 2D-spectrum following Gaussian filtering and 2D-Fourier transformation.

Isolation of sirutekkone. 10 kg of powdered roots of *P. herbacea* were extracted (× 3) in 20 l C_6H_6. The C_6H_6 extracts were combined and evapd *in vacuo* to a dry residue (240 g) which on chromatography on silica gel yielded β-sitosterol and stigmasterol. The plant residue left behind was extracted with three 20 l vols of Me_2CO. The combined Me_2CO extract, on removal of the Me_2CO *in vacuo* gave a residue weighing 90.8 g which was digested with CH_2Cl_2. The soluble portion weighing 20 g was chromatographed on silica gel. Sirutekkone was eluted by EtOAc–hexane (1:4). The material was rechromatographed on silica gel and purified by repeated crystallization from EtOAc–hexane. Yield 0.02%. The pure sample had R_f 0.6 on a silica plate (EtOAc–hexane, 3:7). Mp 214°; $[\alpha]_D^{25}$ +168° ($CHCl_3$) (calcd C 73.17%, H 7.32%; found C 73.17%, H 7.55%; $C_{20}H_{24}O_4$); MS *m/z* 328 [M^+], 285, 271, 243, 127, 83, 43: UV λ_{max}^{EtOH} nm (log ε): 388 (4.52), 217 (4.21), IR λ_{max}^{KBr} cm^{-1}: 3400, 1745, 1610, 1325 and 1315; ^{1}H NMR: δ2.56, 2.52 (H-3), 6.15 (*d*, J = 8.6 Hz, H-6), 6.52 (*d*, J = 8.6 Hz, H-7), 3.68 (*d*, J = 15.4 Hz, H-10a), 2.89 (*d*, J = 15.4 Hz, H-10b), 7.28 (*s*, H-11), 6.80 (*s*, H-14), 3.10 (*m*, H-15), 1.20 (*d*, J = 1.7 Hz, H-16 or H-17), 1.13 (*d*, J = 1.7 Hz, H-16 or H-17), 1.35 (*s*, H-18 or H-19), 1.28 (*s*, H-18 or H-19) and 1.43 (*s*, H-20); ^{13}C NMR: Table 1.

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