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THREE 9,19-CYCLOTETRACYCLIC TRITERPENES FROM *SKIMMIA WALLICHII*

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Key Word Index—*Skimmia wallichii*; Rutaceae; 9,19-cyclotetracyclic triterpenes; skimmiwallichin; skimmiwallinin; skimmiwallin.

Abstract—Phytochemical studies on *Skimmia wallichii* resulted in the isolation of skimmiwallichin, skimmiwallin and a new cycloartanol type compound skimmiwallinin. The structure of skimmiwallinin is elucidated as 3β-methoxy-24-methyl-24-ethyl-9,19-cyclolanost-25(26)-ene on the basis of spectral studies. The structures of skimmiwallichin and another tetracyclic triterpene, now named skimmiwallin, were revised and established to be 3β-methoxy-24,24-diethyl-9,19-cyclolanost-25(26)-ene and 3β-methoxy-25-ethyl-9,19-cyclolanost-24(24^1)-ene, respectively. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Skimmia wallichi Hook. f. et Thoms. ex Gamble is a small shrub growing in Nepal and Sikkim. From this plant, the isolation of taraxerone and the tetracyclic triterpene skimmiwallichin ($C_{35}H_{60}O$) was reported [1] in 1977. The proposed tentative structure **1** for skimmiwallichin was based on its 100 MHz ^{1}H NMR spectrum, mass spectral studies of metastable decays and chemical evidence. The isolation of a second tetracyclic triterpene ($C_{34}H_{58}O$), now named skimmiwallin, was described [2] in 1989 and structure **2** was assigned to it. However, based on the evidence reported below the structures of skimmiwallichin and skimmiwallin have to be revised to **3** and **4**, respectively. In addition, we describe the isolation and structure elucidation of a third tetracyclic triterpene skimmiwallinin ($C_{34}H_{58}O$) which has the structure (**2**) originally ascribed to skimmiwallin.

A detailed and concerted application of 1D and 2D NMR methods and MS studies on the structures of the three compounds was undertaken. Despite the overcrowding of both the ^{13}C and ^{1}H NMR spectra and a nearly exact degeneracy of some ^{1}H chemical shifts, ^{1}H and ^{13}C assignments were successfully carried out using NOED, DFQ-COSY, HOHAHA, ROESY, ^{1}H,^{13}C-HMQC and ^{1}H,^{13}C-long-range coupling correlation (HMBC, COLOC) experiments. As a result, the unusual structure **3** was established for skimmiwallicin, structure **4** for skimmiwallin and structure **2** for the new compound skimmiwallinin.

RESULTS AND DISCUSSION

The petrol extract of *S. wallichii* (whole plant) upon chromatography on an $AgNO_3$-impregnated silica gel column and prep. TLC on $AgNO_3$-impregnated silica gel plates (see Experimental) afforded skimmiwallichin (**3**), skimmiwallinin (**2**) and skimmiwallin (**4**).

The cycloartenol skeleton of these three compounds was indicated by the methyl signals in their NMR spectra (Table 1) and by the characteristic fragment ions in their EI (70 eV) mass spectra: **h** formed by cleavage of the cyclopropane ring and ring B (loss of ring A), **d** $[M - MeOH - 43]^+$ and **e** $[M - MeOH - 69]^+$ [3, 4]. Other ions are due to the loss of MeOH, Me and/or the side chain either from $M^{+\cdot}$ or from **h**: **a** $[M - Me]^+$, **b** $[M - MeOH]^{+\cdot}$, **c** $[M - MeOH - Me]^+$, **d** $[M - MeOH - 43]^+$ and **e** $[M - MeOH - 69]^+$, **g** $[M - \text{side chain}]^+$, **i** $[\mathbf{g} - MeOH]^+$, **m** $[\mathbf{h}\text{-side chain}]^+$, **j** $[\mathbf{i} - 2H]^+$ and **n** $[\mathbf{m} - 2H]^+$ [5]. The observation that peaks at *m/z* 329 (**g**), *m/z* 297 (**i**), *m/z* 295 (**j**), *m/z* 203 (**k**), *m/z* 201 (**l**) and *m/z* 175 (**m**) are common to the spectra of the three compounds indicated that they possess the same 9,19-cyclotetracyclic ring system and differ only in their side chains. The appearance of ions **h** at *m/z* 328 for the two isomeric compounds **2** and **4** suggested different structures for their $C_{11}H_{21}$ side chains.

A complete and unambiguous structural assignment

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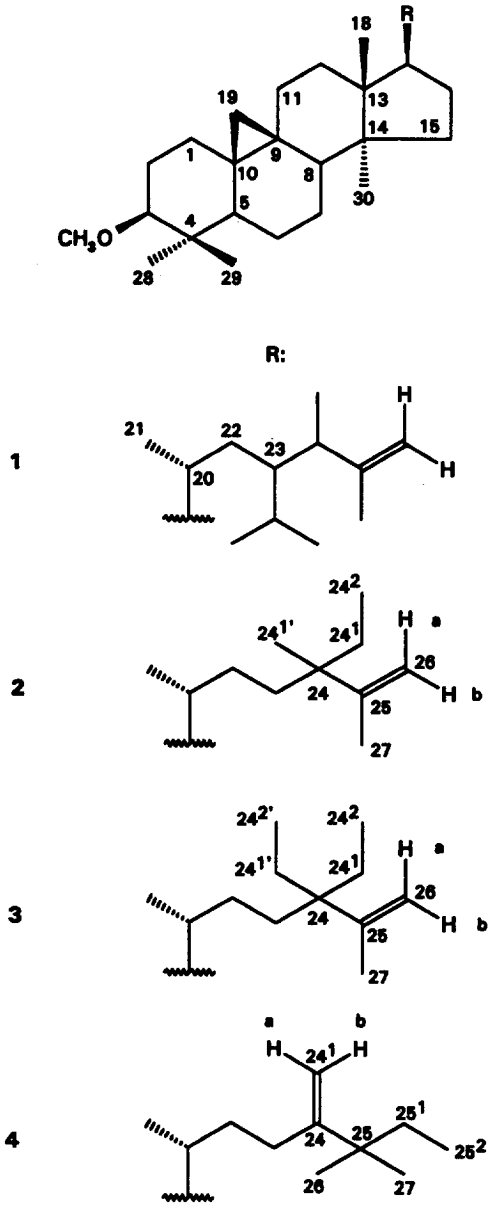


for the three compounds was undertaken to prove their common skeleton and then to find the structures of their side chains. Due to overcrowding in some regions of the ^1H (300 MHz)- and ^{13}C (75 MHz)-NMR-spectra a combination of standard 1D-(DEPT, NOED) and 2D-($^1H,^1H$-COSY, HOHAHA, ROESY, $^1H,^{13}C$-COSY) experiments were run to achieve this task. Most of the structural data were derived from the observation of heteronuclear long-range couplings using $^{13}C,^1H$-COLOC for **3** and $^1H,^{13}C$-HMBC for **2** and **4**.

Skimmiwallinin and skimmiwallin, isomeric compounds of molecular formula $C_{34}H_{58}O$, as determined by mass spectrometry (exact mass found 482.449, calculated 482.446), were isolated as colourless crystals. Their NMR data (Table 1 and Scheme 1) related to the tetracyclic ring system were almost identical. For this reason the discussion below concerning the cyclic part of their structures will be exemplified using the data of skimmiwallin (**4**) only. The ^1H NMR spectra revealed a methoxy group attributable to the C-3β_{eq} position, similar to the usual triterpene methyl ethers, i.e. δ 3.35 *s* (OMe, δ_C 57.63) and δ 2.70 (H-3α_{ax}, δ_C 88.54). In the COSY-spectrum, H-3α (*dd*, J = 11.0 and 4.5 Hz) showed coupling cross peaks to the two proton resonances of a methylene group, assigned to H-2α (δ 1.90) and H-2β (δ 1.43, δ_C 25.44). In the HOHAHA spectrum two cross peaks δ 2.70/1.25, 2.70/1.44 allowed the assignment of the methylene protons at C-1 (δ_C 31.82).

In the HMBC spectrum, the correlations from the Me-28 (δ 0.93) and Me-29 (δ 0.77) protons to the methine carbons at δ 88.54 (C-3) and at δ 47.66 (assigned to C-5) and a quaternary carbon at δ 40.48 (C-4) were found. The same spectra contained correlations from the H-19 endo (δ_H 0.54) and H-19 exo (δ_H 0.31) to the methylene carbons at δ 31.82 (C-1) and δ 26.52 (C-11), the methine carbons at δ 47.97 (C-8, δ_H 1.49) and δ 47.66 (C-5, δ_H 1.26), and two quaternary carbons at δ 19.98 and δ 26.29. These quaternary carbons must be C-9 and C-10.

Intensive NOE cross peaks, H-19_{endo}/H-8 and H-19_{endo}/H-29, in the ROESY spectrum confirm the axial β-positions of H-8 and Me-29. The HOHAHA spectrum revealed that H-5, H-8 and the protons of two methylene groups (H-6α δ 1.54, H-6β δ 1.26, C6 δ 20.96, H-7α δ 1.05, H-7β δ 1.30, C7 δ 25.97) form a spin-system of 6 protons. Large '*trans*'-coupling constants for H-8/H-7α, H-7α/H-6β and H-6β/H-5 deduced from the DQF-COSY spectrum indicated the axial positions.

In the HMBC spectrum, the protons of Me-30 presented long-range correlations to C-8, a methyl carbon δ 18.0 (C-18, δ_H 0.95), a methylene carbon δ 35.55 (C-15, δ_H 1.27, 1.27) and two quaternary carbons δ 45.30 and 48.83, while H-18 showed correlations to C-30, the same quaternary carbons, as well as to a methylene carbon δ 32.92 (C-12, δ_H 1.61, 1.61) and a methine carbon δ 52.30 (C-17, δ_H 1.60). The quaternary carbons must be C-13 (δ 45.30) and C-14 (δ 48.83). Their assignment was carried out based on the data obtained for cycloartenol in a 2D INADEQUATE experiment [6]. Intensive NOEs for H-18/H-8 and H-18/H-19_{endo} prove the β-position of Me-18 while the lack of a NOE for H-30/H-19 indicates the α-position of Me-30.

The position and resonances of CH_2-11 (δ_C 26.52, δ_H 1.98, 1.11) were confirmed through long-range correlations for H-12/C-11, and H-11β/C-19 and H-11α/C-19. The cross peak δ_H 1.27 (H-15)/δ_C 28.16 allowed the assignment of the remaining methylene carbon of the tetracyclic ring system, i.e. C-16 (δ_H 1.89, 1.28).

The NMR spectra of skimmiwallin suggested the following composition of its $C_{11}H_{21}$ side chain: one methyl group Me-21 (δ_H 0.88, δ_C 18.46) with a $^3J_{H,H}$-coupling of 6.3 Hz to the proton of a methine group CH-20 (δ_H 1.39, δ_C 36.44), two methyl groups showing singlets in the ^1H NMR spectrum at δ 0.99 (δ_C 26.96), a quaternary carbon (δ 39.54), two vinylic protons at

Table 1. ^{1}H- and ^{13}C-NMR chemical shifts of compounds **2**–**4** in $CDCl_3$*

	2		**3**		**4**	
Position	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
1α, β	1.25	31.81	1.26	31.83	1.25	31.82
	1.43		1.52		1.44	
2α(eq)	1.90	25.42	1.91	25.43	1.89	25.44
2β(ax)	1.43		1.50		1.43	
3α(ax)	2.70 *dd* (11.2, 4.5)	88.54	2.70 *dd* (11.1, 4.4)	88.51	2.70 *dd* (11.0, 4.5)	88.54
4	—	40.48	—	40.48	—	40.48
5α(ax)	1.26	47.66	1.28	47.68	1.26	47.66
6α(eq)	1.55	20.94	1.55	20.97	1.54	20.96
6β(ax)	0.76		0.80		0.76	
7α(ax)	1.04	25.96	1.15	26.10	1.05	25.97
7β(eq)	1.30		1.31		1.30	
8β(ax)	1.49	47.94	1.45	47.98	1.49	47.97
9	—	19.98	—	19.97	—	19.98
10	—	26.30	—	26.29	—	26.29
11α,β	1.97, 1.11	26.52	1.98, 1.11	26.53	1.98, 1.11	26.52
12α,β	1.59, 1.59	32.88	1.61, 1.61	32.87	1.61, 1.61	32.92
13	—	45.25	—	45.24	—	45.30
14	—	48.81	—	48.81	—	48.83
15	1.26, 1.26	35.55	1.28, 1.28	35.57	1.27, 1.27	35.55
16α,β	1.86, 1.25	28.16	1.91, 1.26	28.23	1.89, 1.28	28.16
17	1.57	52.23	1.57	52.19	1.60	52.30
18	0.93	17.94	0.96	17.92	0.95	18.00
19 endo	0.53 (4.2)	29.83	0.52 (4.1)	29.87	0.54 (4.1)	29.86
19 exo	0.29 (4.2)		0.32 (4.1)		0.31 (4.1)	
20	1.30	36.62	1.31	36.79	1.39	36.44
21	0.84 *d* (6.5)	18.46	0.85 *d* (6.9)	18.59	0.88 *d* (6.3)	18.46
22	1.24†	30.20	0.80, 1.18	29.59	1.14, 1.59	36.04
23	1.54†	36.34	1.11, 1.45	30.37	1.79, 2.04	27.70
24	—	42.06	—	44.41	—	156.76
24^{1}	1.23, 1.44	32.26	1.35, 1.35	25.99	4.75 (24^{1}a), 4.77 (24^{1}b)	107.49
24$^{1'}$	0.93	22.18	1.35, 1.35	25.99	—	—
24^{2}	0.69 t (7.4)	8.38	0.64 *t* (7.5)	7.87	—	—
24$^{2'}$	—	—	0.65 *t* (7.3)	7.87	—	—
25	—	150.27	—	158.30	—	39.54
25^{1}	—	—	—	—	1.36	33.28
25^{2}	—	—	—	—	0.69 *t* (7.6)	9.01
26	4.60 (26a), 4.78 (26b)	111.08	4.66 (26a), 4.89 (26b)	112.00	0.99	26.96
27	1.61	19.30	1.63	19.53	0.99	26.96
28α(ax)	0.93	25.50	0.95	25.53	0.93	25.52
29β(eq)	0.77	14.78	0.79	14.79	0.77	14.78
30	0.86	19.30	0.87	19.30	0.88	19.30
31	3.34	57.63	3.36	57.60	3.35	57.63

δ (ppm) relative to TMS.

* Figures in parentheses are coupling constants in Hz.

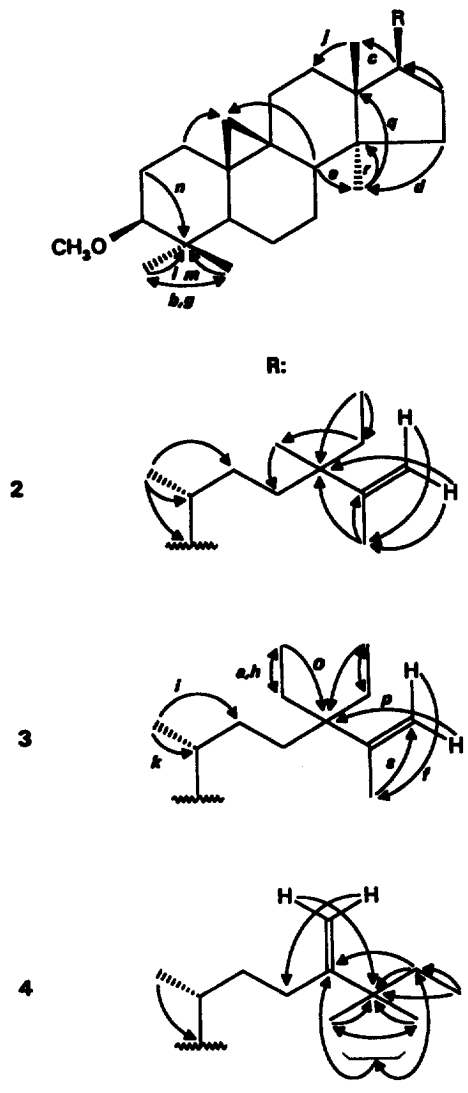
†Not clearly observed.

δ 4.75 and 4.77 (methylene carbon at δ 107.49 and a quaternary carbon at δ 156.76), and two methylene groups with δ_C 36.04 and δ_C 27.70.

Long range correlations (Scheme 1) observed in the HMBC spectrum from both vinylic protons to the quaternary carbon at δ 156.76 (C-24) as well as from δ 4.77 (H-24^{1}b) to the methylene carbon at δ 27.70 (C-23), and from δ 4.75 (H-24^{1}a) to the quaternary carbon at δ 39.54 (C-25) required that C-23 and C-25 were adjacent to C-24. Correlations from the protons of the ethyl group and the two methyl groups Me-26,27 (δ_H 0.99) to the quaternary carbon C-25 showed that these groups are bound to C-25. Long range correlations from the protons of the two methyl groups Me-26,27 to each others carbon and to C-24, C-25 and C-25^{1} supported the proposed arrangement as well as NOE cross peaks H-24^{1}a/H-22 and H-24^{1}b/(H-26 and/or H-27) found in the ROESY spectrum.

Based on these data, the previously proposed structure **2** could be ruled out and structure **4** was unambiguously confirmed for skimmiwallin. This is the first example of the occurrence of a 9,19-cyclotetracyclic triterpene containing one ethyl and two methyl groups attached to a quaternary carbon at the end of its $C_{11}H_{21}$ side chain.

The structure of the $C_{11}H_{21}$ side chain of skim-



Scheme 1. ^{1}H, ^{13}C-long range correlations of skimmiwallichin (**3**) and side chains of skimmiwallinin (**2**) and skimmiwallin (**4**).

miwallinin **2** was also deduced from its NMR spectra, which gave evidence for one methyl group, Me-21 (δ_H 0.84, δ_C 18.46, $^{3}J_{H,H}$ = 6.5 Hz), bound to a methine carbon CH-20 (δ 36.62, δ_H 1.35), two methyl groups with singlets in the ^{1}H NMR spectrum at δ 0.93 (δ_C 22.18) and 1.61 (δ_C 19.30), one ethyl group [methyl triplet at δ 0.69 (δ_C 8.38), coupled to a methylene group at δ 1.23, 1.44 (δ_C 32.26)], two vinylic protons at δ 4.60 and 4.78 (methylene carbon at δ 111.08 and quaternary carbon at δ 150.27), a quaternary carbon δ 42.06 and two methylene groups with δ_C 36.34 and 29.69. The positions of these units in the side chain of skimmiwallinin were confirmed by its HMBC data (Scheme 1).

Long range correlations from the methyl protons δ 1.61 (H-27) to the olefinic methylene carbon δ 111.08 (C-26) and the quaternary carbons at δ 150.27 (C-25) and 42.06 (C-24) indicated an isopropylene group at the end of the side chain. Correlations from the methyl protons of the ethyl group to C-24 and from the methyl protons δ 0.93 (H-24$^{1'}$) to C-24 and the methylene carbon with δ 36.34 (C-23) showed the connectivities at C-24. The position of CH_2-22 (δ_C 30.20) could be elucidated by a correlation cross peak H-21/C-22.

Thus the structure **2** was established for skimmiwallinin which is a a new 9,19-cyclotetracyclic triterpene of biogenetic importance. It could be considered as the missing intermediate from which the steroidal compound 24-ethyl-4α,14α,24-trimethyl-9,19-cyclocholest-25-ene-3β-ol *p*-hydroxycinnamic acid ester [7] is derived.

The molecular formula of $C_{35}H_{60}O$ for skimmiwallichin was confirmed by its mass spectrum (exact mass found 496.463, calculated 496.464 u), ^{1}H, ^{13}C and DEPT spectra. The 300 MHz ^{1}H NMR spectrum revealed the presence of the diagnostic pair of doublets at δ 0.32 and 0.52 for the 9,19-cyclopropane function, a methoxy group at δ 3.36, two vinylic protons at δ 4.66 and 4.89, a vinylic methyl group at δ 1.63, two methyl triplets at δ 0.64 and 0.65 (J = 7.5 and 7.3 Hz respectively), one methyl doublet δ 0.85 and four methyl singlets at δ 0.79, 0.87, 0.95 and 0.96. The presence of an isopropyl group could be ruled out. Instead, the presence of two ethyl groups was proved by correlation cross peaks in the $^{1}H,^{1}H$-COSY spectrum from the methyl triplets at δ 0.64 and 0.65 to the methylene protons at δ 1.35 [q, 4H, 24^{1}-CH_2 (δ_C 25.95) and 24$^{1'}$-CH_2 (δ_C 25.95)].

A careful comparison of the spectral data of the three compounds was undertaken. It was found that the ^{1}H, ^{13}C, $^{1}H,^{1}H$-COSY and $^{1}H,^{13}C$-COSY data of **3** as related to its ring system agreed well with those of **2** and **4**. These data, in addition to the heteronuclear long range correlations observed in a COLOC experiment (Scheme 1), permitted the complete assignment of carbons and protons of the tetracyclic nucleus. The structure elucidation of the $C_{12}H_{23}$ side chain of skimmiwallichin was based on the multiplicity of the remaining ^{13}C signals, the ^{1}H chemical shifts and multiplicity of the remaining unassigned four methyl groups, i.e. one singlet at δ 1.63, one doublet at δ 0.87 and two triplet signals at δ 0.64 and 0.65, as well as the vinylic protons at δ 4.66 and 4.89. In the COLOC spectrum the vinylic protons and vinylic methyl protons show cross peaks with a quaternary carbon at δ 44.41 (Scheme 1). Further, the COLOC's cross peaks ***a***, ***o*** and ***h*** were used to assign an α-position to the methyl vinylic moiety, and the cross peaks ***k*** and ***i*** to assign the C-20–C-22 part of the chain. It was evident from these results that two ethyl groups are located at position C-24 in the side chain of skimmiwallichin. Therefore, structure **1** was ruled out and structure **3** is assigned unambiguously to this compound. This is the first report for the occurrence of a triterpene methyl ether with a 9,19-cyclotetracyclic structure having 34 carbons in its skeleton and carrying two ethyl groups at C-24.

Linked scan measurements at constant B/E of ions **h**

demonstrated characteristic fragmentations by McLafferty rearrangement [8] depending on the position of the double bond in the side chains, i.e. *m/z* 230 for **2** ($-C_7H_{14}$) and **3** ($-C_8H_{16}$) and *m/z* 216 for **4** ($-C_8H_{16}$).

The origin of fragments at *m/z* 175, observed in the spectra of all cycloartanol type tetracyclic triterpenes so far described in the literature [3], has always been associated with a loss of side chains from ions **h** only. It is worth mentioning that B^2/E scans of the *m/z* 175 ions of compounds **2–4** revealed their formation not only from ions **h**, but also from M^+ and from other fragment ions.

2 and **4** are related by a Wagner–Meerwein rearrangement of the ethyl group. It would not be surprising if similar isomers of **3** (e.g. 25-ethyl,24-ethylidene) were found in future.

EXPERIMENTAL

General. Mps: uncorr; IR: BRUKER IFS 113V in KBr disks. TLC: aluminium sheets, silica gel 60 (Merck). The 1D and 2D NMR spectra of **2** and **4** were measured on a BRUKER AC 300 using a 5 mm inverse probe. HOHAHA, ROESY, DQF-COSY were acquired with a size of 2K × 512 data points. After 4 dummy scans 8 scans (HOHAHA), 64 scans (ROESY), and 16 scans (DQF-COSY) were used for each experiment. Mixing times were 40 ms for HOHAHA and 200 ms for ROESY. For processing $\pi/3$ phase shifted sinesquared window function was applied in both dimensions and zero filling to gain real data matrices after Fourier transformation of 2k × 512 for HOHAHA and ROESY and 1k × 1k for DQF-COSY. The HMQC experiment with BIRD pulse sequence and GARP decoupling during acquisition was acquired with a size of 2K × 256 data points. A $\pi/2$ phase-shifted sinesquared window function was used in both dimensions and zero-filling before Fourier transformation to gain a matrix of 2K × 512W real data points. For the non-decoupled HMBC experiment optimized to a long-range coupling constant around 10 Hz through an evolution delay of 50 ms, 512 experiments with 2k data points in t2 and 48 scans after 4 dummy scans were perormed. For processing a $\pi/3$ shifted sine window function was applied in both dimensions and zero filling to gain a matrix of 2k × 1k real data points after Fourier transformation.

1D and 2D NMR spectra of **3** were measured at 250.16 MHz (^1H) and 62.90 MHz (^{13}C) on a BRUKER WM-250 equipped with an Aspect 2000 computer and a 5 mm $^1H/^{13}C$ dual probehead. All chemical shifts were referenced to the solvent ($CDCl_3$) peaks: 7.25 ppm for ^1H and 77.00 ppm for ^{13}C. The standard DEPT-135° was used to provide full information about the number of C-attached protons. The 1D nuclear Overhauser effect difference (NOED) spectra were measured with an irradiation time of 0.7 s and delay of 7 s. The COSY experiment was performed using the standard pulse sequence. The standard 2D $^1H,^{13}C$-COSY spectra were recorded as a matrix of 64 × 2048 points with a delay of 3.33 and 2.22 ms. Zero fillings was done in the F1 (^1H) domain and a sine-bell nonshifted weighting was used in both dimensions. The COLOC experiment was performed with the original program using 128 steps in the phase cycling with D1 = 20 ms [1/3 ($^3J_{H,H}$, $^3J_{H,H}$ = 16.6 Hz] and Δ2 = 25 ms [1/3($^3J_{HC}$), $^3J_{HC}$ = 13.3 Hz]. The acquired data matrix was 72 × 2K and the transformed matrix was 512 × 2K. A shifted square sine-bell function was employed in F2 and a nonshifted sine-bell function in F1.

Mass spectral measurements were performed with a HSQ-30 instrument (FINNIGAN-MAT).

Plant material. Skimmia wallichii (Rutaceae) (entire herb) was collected in Nepal in 1974. A voucher specimen is deposited in the herbarium of the Department of Botany, Delhi University.

Isolation of compounds. The air-dried material (2 kg) of *S. wallichii* was extracted with hot petrol (5 × 3 l). The combined petrol extracts were concd to a small vol. under red. pres. The yellow concentrate (3 g) was subjected to CC on silica gel to give frs A–E. Fr. A (1 g) on crystallization from $CHCl_3$–MeOH gave solid F (0.230 g) and mother liquors G (0.70 g). The solid F on chromatography over a $AgNO_3$-impregnated silica gel column gave pure skimmiwallichin (**3**, 200 mg). The mother liquors G (50 mg) were subjected to prep. TLC on $AgNO_3$-impregnated silica gel plates (multiple development) using as solvent system hexane–$CHCl_3$ (2:1) to give skimmiwallicin (**3**, 10.0 mg), skimmiwallinin (**2**, 2.0 mg) and skimmiwallin (**4**, 11.0 mg), described in order of their increasing polarity. Further purification was achieved by repeated crystallization of the isolated compounds from MeOH.

Skimmiwallinin (**2**). Mp 141–144°. IR ν_{max}^{KBr} cm^{-1}: 1630, 1189 and 886; EIMS, 70 eV, *m/z* (rel. int.): 482 $[M]^+$ (25), 467 (**a**, 16), 450 (**b**, 100), 435 (**c**, 47), 407 (**d**, 42), 381 (**e**, 17), 329 (**g**, 10), 328 (**h**, 25), 297 (**i**, 13), 295 (**j**, 1), 230 (13), 203 (**k**, 33), 201 (**l**, 21), 175 (**m**, 46), 173 (**n**, 25).

Skimmiwallichin (**3**). Mp 156–159°. ν_{max}^{KBr} cm^{-1}: 1633, 1188 and 890; EIMS, 70 eV, *m/z* (rel. int.): 496 $[M]^+$ (21), 481 (**a**, 13), 464 (**b**, 100), 449 (**c**, 33), 421 (**d**, 29), 395 (**e**, 17), 342 (**h**, 21), 297 (**i**, 10), 295 (**j**, 1), 230 (17), 203 (**k**, 23), 201 (**l**, 13), 175 (**m**, 33), 173 (**n**, 15).

Skimmiwallin (**4**). Mp 139–143°. IR ν_{max}^{KBr} cm^{-1}: 1633, 1188 and 890; EIMS, 70 eV, *m/z* (rel. int.): 482 $[M]^+$ (17), 467 (**a**, 22), 450 (**b**), 100), 435 (**c**, 37), 407 (**d**, 33), 381 (**e**, 22), 328 (**h**, 17), 297 (**i**, 15), 295 (**j**, 1), 216 (39), 203 (**k**, 48), 201 (**l**, 30), 175 (**m**, 48), 173 (**n**, 30).

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