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A *SECO*-CYCLOARTANE FROM *ILLICIUM VERUM*

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Key Word Index—*Illicium verum*; Illiciaceae; *seco*-cycloartane; chemotaxonomy; 2D-NMR.

Abstract—The dichloromethane extract of the leaves of *Illicium verum* yielded the ring A-cleaved *seco*-cycloartane: 3,4-*seco*-(24*Z*)-cycloart-4(28),24-diene-3,26-dioic acid, 26-methyl ester, which is the 26-methyl ester of nigranoic acid. The structure of the new compound was deduced by 2D-NMR spectroscopy, which demonstrated conclusively that it is isomeric with the 3-methyl ester of nigranoic acid recently reported from *Illicium dunnianum*. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Illicium verum Hook f. (Chinese star anise) is an evergreen tree indigenous to southern China, which is used by local people as a stimulant and carminative [1]. It is easily confused with the extremely posionous *I. anisatum*, which is found in the same geographical region and which produces morphologically similar fruits [2]. Previous chemical investigations of *I. verum* have yielded 4-ethoxyphenol, anisyl ketone [3], the phenylpropanoid, anisoxide [4] and the sesquiterpenes, veranisatins A and B [5].

RESULTS AND DISCUSSION

Extraction of the aerial parts of *I. verum* yielded the novel *seco*-cycloartanedioic acid 26-methyl ester (**1**). HREIMS established the formula of **1** as $C_{31}H_{48}O_4$. 2D-NMR experiments, HSQC (Table 1) and HMBC (Fig. 1), were used to confirm the *seco*-cycloartane skeleton of **1**, and in particular demonstrated conclusively that the methyl ester was located at the 26-position rather than the 3-position. Full NMR assignments were confirmed by the ^{1}H-^{1}H COSY spectra (not shown). The *Z* stereochemistry at the double bond was deduced by observation of a strong correlation between H-27 (δ_H 1.90) and H-24 (δ_H 5.93) in NOESY spectra. The extract also contained the known cycloartane, schizandronic acid (**2**) [6]. 3,4-*seco*-Cycloartanes such as **1** would seem to be biogenetically derived from 3-keto-cycloartanes such as **2** by oxidative cleavage at the 3,4-bond.

Compound **3**, the isomeric 3-methyl ester of **1**, has recently been reported as a constituent of *I. dunnianum* [7]. Both the parent compound, nigranoic acid (**4**), and the 3,26-dimethyl ester of nigranoic acid (**5**) are known from *Schisandra nigra* [8] and *Tillandsia usneoides* respectively [9]. This is the second reported occurrence of cycloartanes and *seco*-cycloartanes from the genus *Illicium*, and supports the suggestion made previously that the extremely rare 3,4-*seco*-cycloartane class of triterpenes [10] be regarded as a chemotoxonomic marker for the Illiciales family. The previous report was from *I. dunnianum*; both species are members of the section Cymbostemon (Spach) A. C. Sm.

EXPERIMENTAL

General

NMR: Bruker DRX 500 and TMS with $CDCl_3$ as solvent and TMS as int. standard. HSQC and HMBC experiments were recorded with 2048 data points in F_2 and 128 data points in F_1. EIMS: 70 ev; FTIR: CHCl3; TLC; compounds located using *p*-anisaldehyde; HPLC: PREP-SIL 20 mm × 25 cm column, flow rate 8 ml/min.

Leaf tissue of *I. verum* (1.2 Kg) was obtained from the South China Botanical Garden (accession 850117; material originally collected in Guangxi province by the Guangxi Institute of Botany); a voucher specimen (Hao Gang 103) has been deposited in the herbarium of the University of Hong Kong (KHU). The sample was ground to a fine powder under liq. N_2 and immediately extracted with CH_2Cl_2. The organic extract was then dried and evapd. under red. pres. to yield a dark green oil (26.5 g; 2.2% w/w) which was separated chromatographically. **1** (46.4 mg) by CC (EtOAc-hexane, 1:1) followed by HPLC (R_t 13.1 mins in EtOAc-hexane-AcOH, 18:81.5:0.5); **2** (21.4 mg) by

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Table 1. NMR assignments for compound **1** ($CDCl_3$)

Assignment	δ_C	δ_H	Assignment	δ_C	δ_H
1	28.9	2.07, 1.38	16	28.1	1.92, 1.29
2	31.1	2.54, 2.29	17	52.2	1.59
3	178.1	—	18	18.1	0.96
4	149.4	—	19	30.0	0.73, 0.41
5	45.9	2.43	20	36.0	1.41
6	27.8	1.51, 1.08	21	18.0	0.89
7	25.0	1.31, 1.10	22	35.9	1.53, 1.13
8	47.7	1.57	23	26.7	2.50, 2.38
9	21.5	—	24	144.0	5.93
10	27.0	—	25	126.5	—
11	27.0	2.10, 1.26	26	168.6	—
12	33.0	1.65, 1.65	27	20.7	1.90
13	45.2	—	28	111.6	4.82, 4.74
14	49.0	—	29	19.8	1.69
15	35.6	1.28, 1.28	30	19.8	0.93
			26-OMe	51.2	3.74

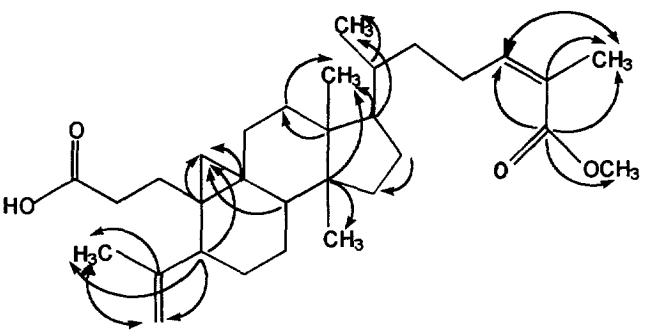
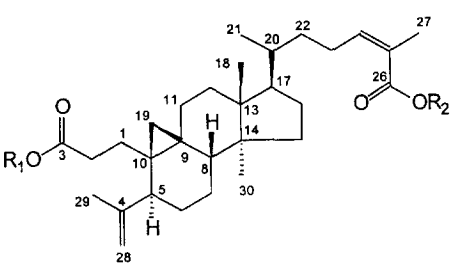
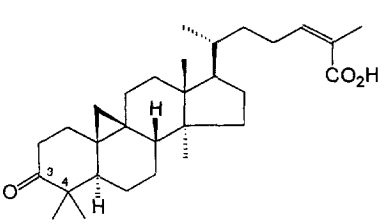


Fig. 1. HMBC correlations for **1** (arrows represent correlations from ^{13}C to ^{1}H).





1 R_1 = H; R_2 = Me

2

3 R_1 = Me; R_2 = H

4 R_1 = H; R_2 = H

5 R_1 = Me; R_2 = Me

CC (EtOAc-hexane, 1:1) followed by HPLC (R_t 12.6 mins in EtOAc-hexane-AcOH, 18:81.5:0.5).

3,4-*seco*-(24*Z*)-*cycloart*-4(28),24-*diene*-3,26-*dioic acid*, 26-*methyl ester* (**1**)

Solid.$[\alpha]_D$ +17.9° ($CHCl_3$, *c* 1.2). HREIMS *m/z* (rel. int.): 484.3552 ([M^+] Δ 0.1 mmu for $C_{31}H_{48}O_4$) (20), 469 (50), 454 (100), 439 (35), 436 (25), 355 (65), 316 (55), 313 (80), 301 (20), 261 (20), 249 (25), 235 (55), 217 (20), 201 (25), 175 (60), 161 (55), 133 (45), 107 (60); IR υ_{max} $CHCl_3$ cm^{-1}: 3400–2400 br, 3028, 2947, 2872, 1697, 1638, 1458, 1383; ^1H NMR: δ 5.93 (1H, *t*, *J*=6.5 Hz), 4.82 (1H, *s*), 4.74 (1H, *s*), 3.74 (3H, *s*), 1.90 (3H, *s*), 1.69 (3H, *s*), 0.96 (3H, *s*), 0.93 (3H, *s*), 0.89 (3H, *d*, *J*=6.5 Hz), 0.73 (3H, *d*, *J*=4.3 Hz), 0.41 (3H, *d*, *J*=4.3 Hz).

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