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2′,3′-DEHYDROSALANNOL, A TETRANORTRITERPENOID FROM *AZADIRACHTA INDICA* LEAVES*

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Key Word Index—*Azadirachta indica*; Meliaceae; leaf; 2′,3′-dehydrosalannol; senecioxy ester; tetra-nor-triterpenoid.

Abstract—2′,3′-Dehydrosalannol, a new meliacin related to salannin, has been isolated from the leaves of *Azadirachta indica* and characterized as 2′,3′-dehydrosalannol on the basis of its spectral data.

In a previous communication, we reported on the isolation of a new flavanone, nimbaflavone [1], along with the known tetra-nor-triterpenoids nimbolide [1, 2] and 3-deacetylsalannin [1, 3], from the chloroform-soluble fraction of the alcoholic extract of *Azadirachta indica* A. Juss leaves which has shown hypotensive activity. Careful chromatography of the chloroform-soluble fraction over a neutral alumina column yielded a new meliacin, 2′,3′-dehydrosalannol (**1**), along with more sitosterol and the β-D-glucoside of β-sitosterol.

The M_r ($[M]^+$ at m/z 554, $C_{32}H_{42}O_8$) and the various functional groups present in 2,3-dihydrosalannol (**1**), as demonstrated by the IR and NMR spectra, were common to those present in 3-deacetylsalannin (**2**). On acetylation, **1** yielded a non-crystalline acetate (**1a**), $C_{34}H_{44}O_9$ ($[M]^+$ at m/z 596), thus confirming the presence of a free hydroxyl group.

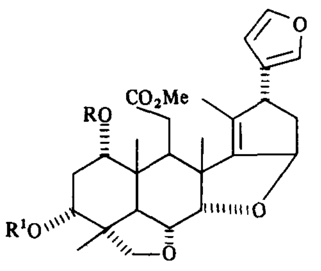
The ^1H NMR spectra of **1** and its acetate (**1a**) were very similar to those of 3-deacetylsalannin (**2**) and salannin (**2a**). In the case of **1**, the olefinic proton (2′-H) of the senecioxy ester group appeared as a narrow quartet at δ5.7 (J = *ca* 1.0 Hz) whereas a multiplet at δ6.9 for the tiglyl ester group was present in **2** [3]. On biogenetic grounds and the identical chemical shift values of the C-19, C-29 and C-30 methyl protons in the ^1H NMR spectra of **1** and **2**, the senecioxy ester groups could be placed at C-1 in **1**. This was further supported on comparison of the ^{13}C NMR spectra of **1** and **2**. The C_5 ester chain in **1** showed signals at δ164.8 (*s*, C-1′), 115.7 (*d*, C-2′), 157.9 (*s*, C-3′), 27.4 (*q*, C-4′/C-5′) and 20.4 (*q*, C-5′/C-4′). This fully supported the presence of a senecioxy ester chain in **1**.

Kraus and Cramer [3] have previously reported the isolation of the dihydro derivative of **1**, salannol, from *A. indica*.

EXPERIMENTAL

Mps (open capillary): uncorr.; IR: KBr; ^1H NMR: 90 MHz, CDCl$_3$, TMS as internal reference; ^{13}C NMR: CFT-20, CDCl$_3$, shifts reported in ppm with respect to TMS. TLC: silica gel, CeSO$_4$ as spray.

Extraction and isolation of 2′,3′-dehydrosalannol (**1**). The air-dried leaves (8 kg) of *A. indica* collected locally (identified by Dr. B. N. Mehrotra; a specimen voucher has been deposited at the herbarium of the Institute) [1] were extracted with 90% EtOH and processed as reported in ref. [1]. The CHCl$_3$ fraction after



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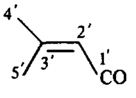
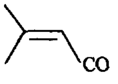
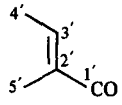
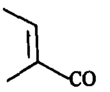
1		H
1a		Ac
2		H
2a		Ac

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separation of nimbolide, sitosterol and nimbaflavone [1] was subjected to CC over neutral alumina (Brockman quality) using C_6H_6–$CHCl_3$ (1:1) as eluant, followed by C_6H_6–$CHCl_3$ (1:3), $CHCl_3$ and finally MeOH. Fractions were monitored by TLC. Earlier fractions on evapn yielded a fresh quantity of sitosterol, mp 120–125°. The $CHCl_3$ fractions were evapd and the residue was crystallized (MeOH–Et_2O) to yield fine needles (255 mg) of 2′,3′-dehydrosalannol (**1**), mp 183–185°, $[\alpha]_D + 180°$. (Found: C, 70.92; H, 7.8. $C_{32}H_{42}O_8$ requires: C, 71.11; H, 7.54%.) IR ν_{max} cm^{-1}: 3410, 2900, 1724, 1710, 1650, 1440, 1390, 1230, 1150, 1080 and 980; ^{1}H NMR: δ0.95 (3H), 1.15 (3H), 1.31 (3H), 1.68 (3H, Me-13), 1.9 (*d*, Me) 2.2 (Me; $>$=CHCO), 2.6–2.8 (3H, *m*), 3.2 (–COOMe), 3.6 (2H, *q*), 4.0 (*dd*, H-6), 4.15 (*d*, H-7), 5.0 (*t*, H-1), 5.4 (1H, *m*), 5.7 (1H, *q*), 6.3 (1H, βH-furan), 7.23 (2H, αH-furan); ^{13}C NMR: δ71.9 (*c*, C-1), 30.6 (*t*, C-2), 71.0 (*d*, C-3), 44.2 (*s*, C-4), 38.9 (*d*, C-5), 72.5 (*d*, C-6), 85.9 (*d*, C-7), 49.0 (*s*, C-8), 39.4 (*d*, C-9), 40.7 (*s*, C-10), 30.4 (*t*, C-11), 172.7 (*s*, C-12), 134.5 (*s*, C-13), 146.0 (*s*, C-14), 87.8 (*d*, C-15), 41.0 (*t*, C-16), 49.4 (*d*, C-17), 13.0 (*q*, C-18), 15.3 (*q*, C-19), 127.1 (*d*, C-20), 138.7 (*d*, C-21), 110.8 (*d*, C-22), 142.7 (*d*, C-23), 77.8 (*t*, C-28), 19.7 (*q*, C-29), 16.9 (*q*, C-30), 154.8 (*s*, C-1′), 115.7 (*d*, C-2′), 157.9 (*s*, C-3′), 20.4 (*q*, C-4′), 27.4 (*q*, C-5′); MS *m/z*: 554 $[M]^+$, 539 $[M-15]^+$, 537 $[M-H_2O]^+$, 472, 471, 454, 453, 283.

2′,3′-Dehydrosalannol acetate (**1a**). **1** (40 mg) in C_5H_5N (0.5 ml) and Ac_2O (0.25 ml) was left overnight at room temp then heated (110°) for 1 hr, poured over crushed ice, and worked up to yield the acetate **1a** (40 mg) which failed to crystallize. IR ν_{max} cm^{-1}: 2900, 1740–1730, 1440, 1380, 1250, 1150, 1050; MS *m/z*: 596 $[M]^+$, 554, 514, 513, 496, 422, 283.

β-Sitosterol-D-glucoside. This glucoside (IR, mmp) was obtained on concn of the MeOH fractions. Acid hydrolysis gave β-sitosterol (mp, mmp, and IR) and glucose (Co-TLC).

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3α,11α-DIHYDROXY-23-OXO-LUP-20(29)-EN-28-OIC ACID FROM *ACANTHOPANAX TRIFOLIATUS**

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Key Word Index—*Acanthopanax trifoliatus*; Araliaceae; triterpenes; 3α,11α-dihydroxy-23-oxo-lup-20(29)-en-28-oic acid.

Abstract—The new triterpene 3α,11α-dihydroxy-23-oxo-lup-20(29)-en-28-oic acid was isolated from *Acanthopanax trifoliatus*. Its structure has been determined on the basis of spectroscopic data and chemical transformations.

INTRODUCTION

In an earlier paper [1], we reported on the isolation and structures of the new triterpenes 3α,11α-dihydroxy-lup-20(29)-en-28-oic acid and its corresponding 3α,11α,23-triol (**3**) from *Acanthopanax trifoliatus* (L.) Merr., a plant with ginseng-like activity [2] which is used in Vietnamese folk medicine. In this communication, we describe a further new lupane derivative from the same source. Based on spectroscopic data and chemical transformations, its structure was elucidated as 3α,11α-dihydroxy-23-oxo-lup-20(29)-en-28-oic acid (**1**).

RESULTS AND DISCUSSION

Compound **1**, $C_{30}H_{46}O_5$ (high-resolution MS), was isolated from the dried leaves of *A. trifoliatus*. Its IR spectrum showed absorptions assignable to hydroxyl, aldehyde, carboxyl and $>C=CH_2$ functions. Its conversion to the methyl ester **2** indicated that it contained one carboxyl function.

The mass spectra of **1** and **2** showed typical fragment ions derivable from ring C cleavages similar to those found for other lupane carboxylic acids [1, 3]. In particular, the presence of ion **a** (*m/z* 251 for **1**) provided evidence for C-11 substitution [4], as well as localization of the aldehyde function at ring A.

The ^{1}H NMR spectrum (acetone-d_6) of **1** showed signals for two secondary hydroxyl groups [δ3.91, 11β-H,

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*Part 13 in the series "Natural Products from Vietnamese Plants". For Part 12 see ref. [1].