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; ^1H 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**).

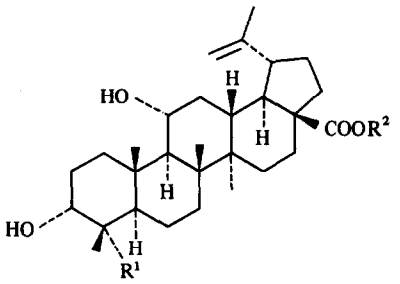
*Part 13 in the series "Natural Products from Vietnamese Plants". For Part 12 see ref. [1].

RESULTS AND DISCUSSION

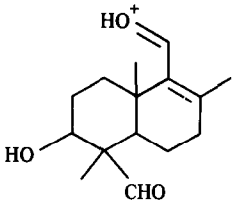
Compound **1**, $C_{30}H_{46}O_5$ (high-resolution MS), was isolated from the dried leaves of *A. trifoliatus*. Its IR spectrum showed absorptions assignable to hydroxyl, aldehyde, carboxyl and >C=CH_2 functions. Its conversion to the methyl ester **2** indicated that it contained one carboxyl function.

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



	R^1	R^2
1	CHO	H
2	CHO	Me
3	CH_2OH	H



a

Table 1. ^{13}C NMR chemical shifts of **1** (50.3 MHz, C_5D_5N, δ values are downfield from TMS: δ (TMS) = δ (C_5D_5N) + 135.5)

C	δ	C	δ
1	35.4* *t*	16	32.8 *t*
2	27.1 *t*	17	56.5 *s*
3	73.1 *d*	18	49.5 *d*
4	53.0 *s*	19	47.5 *d*
5	44.2 *d*	20	150.8 *s*
6	21.3 *t*	21	31.3 *t*
7	35.5* *t*	22	37.4 *t*
8	42.8 *s*	23	209.9 *d*
9	56.0 *d*	24	17.8† *q*
10	39.0 *s*	25	15.0† *q*
11	69.8 *d*	26	16.8† *q*
12	38.3 *t*	27	14.8 *q*
13	37.6 *d*	28	178.8 *s*
14	43.3 *s*	29	110.0 *t*
15	30.1 *t*	30	19.5 *q*

*,†Assignments may be interchanged.

dt, two diaxial (J = 11.0 Hz) and one axial/equatorial (J' = 5.0 Hz) spin-spin couplings [4]; δ3.63, 3β-H, *t*, $J_{AX} + J_{BX}$ = 5.5 Hz], two olefinic protons (δ4.60 and 4.75), one aldehyde proton (δ9.50) and five methyl singlets. One of these methyl singlets was found to be shifted to low-field at δ1.72.

All 30 carbon atoms (Table 1) in the ^{13}C NMR spectrum of **1** were assigned on the basis of the ^{13}C chemical shifts of nepeticin [4], betulinic acid [5] and 3α,11α-dihydroxy-lup-20(29)-en-23,28-dioic acid [6]. These assignments were supported by the observed multiplicities in the single-frequency off-resonance decoupled (SFORD) [7], noise off-resonance decoupled (NORD) [8] and attached proton test (APT) [9] spectra. The absence of a low-field shifted methyl carbon signal (>20 ppm) suggested from increment considerations, including those of the 3α-hydroxydammaranes [10], an untouched axial 4β-methyl function. Therefore, these data indicated the presence of the oxo group at C-23.

From the above-mentioned data for the new triterpenoid acid, the structure **1** can be deduced. This was independently confirmed by sodium borohydride reduction of **1** to the triol **3**, which was identical in all respects (IR, MS, ^1H NMR) with an authentic specimen of **3** obtained earlier [1] from *A. trifoliatus*.

EXPERIMENTAL

The ^1H NMR spectra (100 MHz) were measured in Me_2CO-d_6 with hexamethyldisiloxane (HMDS) as internal standard. The chemical shifts were calculated with respect to TMS by using the equation δ (TMS) = δ (HMDS) + 0.06.

Powdered, air-dried and defatted leaves (200 g) of *A. trifoliatus* (collected near Hanoi in April 1981 and identified by Dr. Ph. V. Nguyen; a voucher specimen has been deposited at the Institute of Biology of the NRC SRV, Hanoi) were extracted exhaustively with MeOH for 6 hr. The solvent was removed *in vacuo* and the residue (40 g) chromatographed on a silica gel column using increasing concns of $CHCl_3$ in petrol as the eluant. Elution with $CHCl_3$ gave 1.4 g (0.7% yield) **1**, mp 215–218° (EtOAc–petrol); $[\alpha]_D^{25}$ −27.2° (*c* 0.34 in EtOH); IR ν_{max}^{nujol} cm^{-1}: 1645 (>C=CH_2), 1690 (COOH), 1725, 2725 (CHO), 3070 (>C=CH_2), 3350 (*br*, OH); MS 75 eV *m/z* (rel. int.): 486.3358 $[M]^+$ (6) ($C_{30}H_{46}O_5$, calc. 486.3345), 468 (34) $C_{30}H_{44}O_4$, 450 (28) $C_{30}H_{42}O_3$, 440 (50) $C_{29}H_{44}O_3$, 422 (50), 385 (28), 285 (14), 251 (a, 23), 234 (100), 218 (50); ^1H NMR: δ0.96, 0.98, 1.10, 1.10 (each 3H, *s*, 24-H_3, 25-H_3, 26-H_3, 27-H_3), 1.72 (*s*, 30-H_3), 3.63 (*t*, $J_{AX} + J_{BX}$ = 5.5 Hz, 3β-H), 3.91 (*dt*, J = 11, J' = 5 Hz, 11β-H), 4.60 and 4.75 (each *m*, 29-H_2), 9.50 (*s*, 23-H); ^{13}C NMR: see text.

Methyl ester **2** was obtained from **1** by treatment with CH_2N_2 in MeOH. Silica gel chromatography afforded, by elution with petrol–$CHCl_3$ (3:7), **2** (yield 75%): mp 75° (dec., Me_2CO–petrol): $[\alpha]_D^{25}$ −22.4° (*c* 0.38 in EtOH); IR ν_{max}^{nujol} cm^{-1}: 1645 (>C=CH_2), 1720 (CHO), 1730 (COOMe), 3075 (>C=CH_2), 3425 (*br*, OH); MS 10–16 eV *m/z* (rel. int.): 500 $[M]^+$ (15), 482 (32), 464 (22), 454 (27), 440 (50), 385 (25), 278 (45), 250 (100), 248 (87), 233 (62); ^1H NMR: δ0.95, 1.04, 1.06, 1.09 (each 3H, *s*, 24-H_3, 25-H_3, 26-H_3, 27-H_3), 1.70 (*s*, 30-H_3), 3.66 (*s*, COOMe), 3.71 (*t*, $J_{AX} + J_{BX}$ = 5.5 Hz, 3β-H), 3.97 (*dt*, J = 11, J' = 5 Hz, 11β-H), 4.63 and 4.76 (each *m*, 29-H_2), 9.53 (*s*, 23-H).

Reduction of **1** *to* **3**. To a soln of **1** (48.6 mg) in 2 ml MeOH was added an excess of $NaBH_4$ (30 mg). After 3 min, HOAc (1 ml) was added. The mixture was evapd and the residue chromatographed. Elution with $CHCl_3$–EtOAc (4:1) gave 34 mg **3** (identical in all respects with authentic material [1]).

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FOETIDIN, A SESQUITERPENOID COUMARIN FROM *FERULA ASSA-FOETIDA*

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Key Word Index—*Ferula assa-foetida*; Umbelliferae; root extract; sesquiterpenoid coumarin; 4-hydroxycoumarin; foetidin.

Abstract—A new sesquiterpenoid coumarin, foetidin, has been isolated from the roots of *Ferula assa-foetida.*

Extracts of *Ferula* spp. are well known in the Mediterranean area as medicines and as food additives (spice). Extracts of *Ferula assa-foetida L.* are used as an anti-spasmodic, a diuretic, a vermifuge and an anti-algetic [1–3]. A characteristic feature of this plant is the presence of sesquiterpenoid coumarins [4]. We now report on a new constituent called foetidin (**1**), which represents a new sesquiterpenoid coumarin.

The dried roots of *F. assa-foetida* were extracted with ethanol–water (19:1) to give a syrup, the fractionation of which by column chromatography yielded foetidin (**1**) as colourless plates, mp 176–178°, $[\alpha]_D^{20}$ −39.8° (ethanol). The compound displayed a behaviour typical of coumarin derivatives in dissolving in dilute alkali from which it was precipitated on addition of an acid. Cleavage by hydroiodic acid in acetic acid gave 4-hydroxycoumarin as shown by cochromatography.

The structure of foetidin was established by comparison of its ^{13}C NMR spectrum with those of colladonin (**2**) [5] and 4-methoxycoumarin (**3**) [6]. The chemical shifts of the coumarin and sesquiterpene moieties agreed well with those of 4-methoxycoumarin and the sesquiterpene moiety of colladonin, respectively. Thus foetidin had the same sesquiterpene moiety (including all stereochemical implications) as colladonin, the sesquiterpene being, however, attached to oxygen at C-4 of coumarin.

The proposed structure is in accord with the IR spectrum (OH band at 3400 cm^{-1}, further bands in the region 1685–1610 cm^{-1} due to different double bonds) and with the UV spectrum (double bands at 265/277 and 303/315 nm typical for 4-alkoxycoumarins [7]). It also agreed well with the ^{1}H NMR spectrum, which revealed an axial C<u>H</u>OH (J = 11.0 Hz), an exocyclic methylene group at δ4.54 and 4.92*, three methyl groups linked with quaternary C atoms at *ca* 1 ppm, a CH_2–O group at δ4.35. A singlet at δ5.72 was typical for a coumarin with an alkoxy group at C-4 [9]. The M_r was established by EI mass spectrometry of the compound and its monoacetate (m/z 382 and 424, respectively). The fragmentation pattern was in agreement with the deduced structure, although the base signal at m/z 163 was due to the coumarin moiety with two additional hydrogens, as shown by accurate mass measurement ($C_9H_7O_3$). The same unusual rearrangement [10] is observed in the spectrum of colladonin (sample kindly provided by Prof. Pinar, Madrid), m/z 163

*The same signals are observed in coladonin which is identical with colladonin [8].