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Delevoyin C, a tetranortriterpenoid from *Entandrophragma delevoyi*

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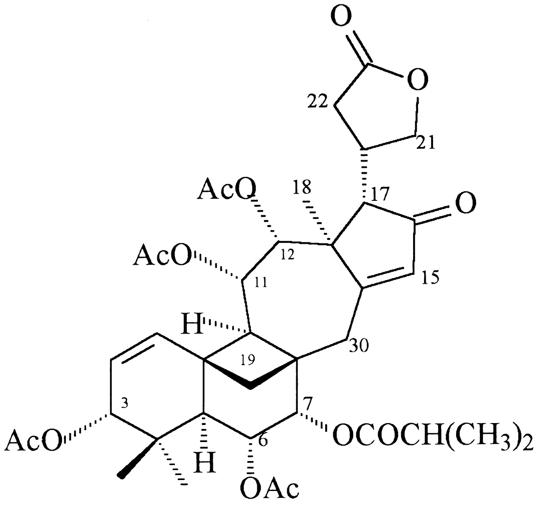
Abstract

The hexane extract of the bark of *Entandrophragma delevoyi* has yielded a novel tetranortriterpenoid, delevoyin C. This compound contains a cyclobutanyl ring incorporating C-19 and a cycloheptanyl ring C including C-30. Gedunin and 11β-Acetoxygedunin were isolated from the hexane extract of the wood. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Entandrophragma delevoyi; Meliaceae; Tetranortriterpenoid; Delevoyin C; 11β-acetoxygedunin; Gedunin

1. Introduction

Entandrophragma delevoyi (de Wild) is a member of the Meliaceae family occurring in Zambia. Plant material was collected from a tree growing on the Kafue Flats and a herbarium specimen was deposited in the Forest Herbarium, Oxford (C Fagg 365). Previous work on the wood of this species has yielded gedunin and sitosterol (Adesida & Taylor, 1967). The hexane extract of the bark of the same specimen has previously yielded azadirone, 14β,15β-epoxyazadirone, 6α-acetoxyazadirone, 6α-acetoxy-14β,15β-epoxyazadirone, 6α-acetoxy-14β,15β-epoxyazadiradione, 3,4-*seco*tirucalla-4(28),7,24-triene-3,21-dioic acid, delevoyin A (3,4-*seco*tirucalla-4(28),7,24-trien-3-oic acid) and delevoyin B (6α- acetoxykihadalactone) (Mulholland, Osborne, Roberts & Taylor, 1994). The hexane extract of the bark has now yielded a further triterpenoid derivative, delevoyin C. The hexane extract of the wood has yielded the known limonoid, 11β-acetoxygedunin which has been reported once previously from *Carapa guyanensis* (Connolly, Mc Crindle, Overton & Feeney, 1966), and the common limonoid, gedunin.



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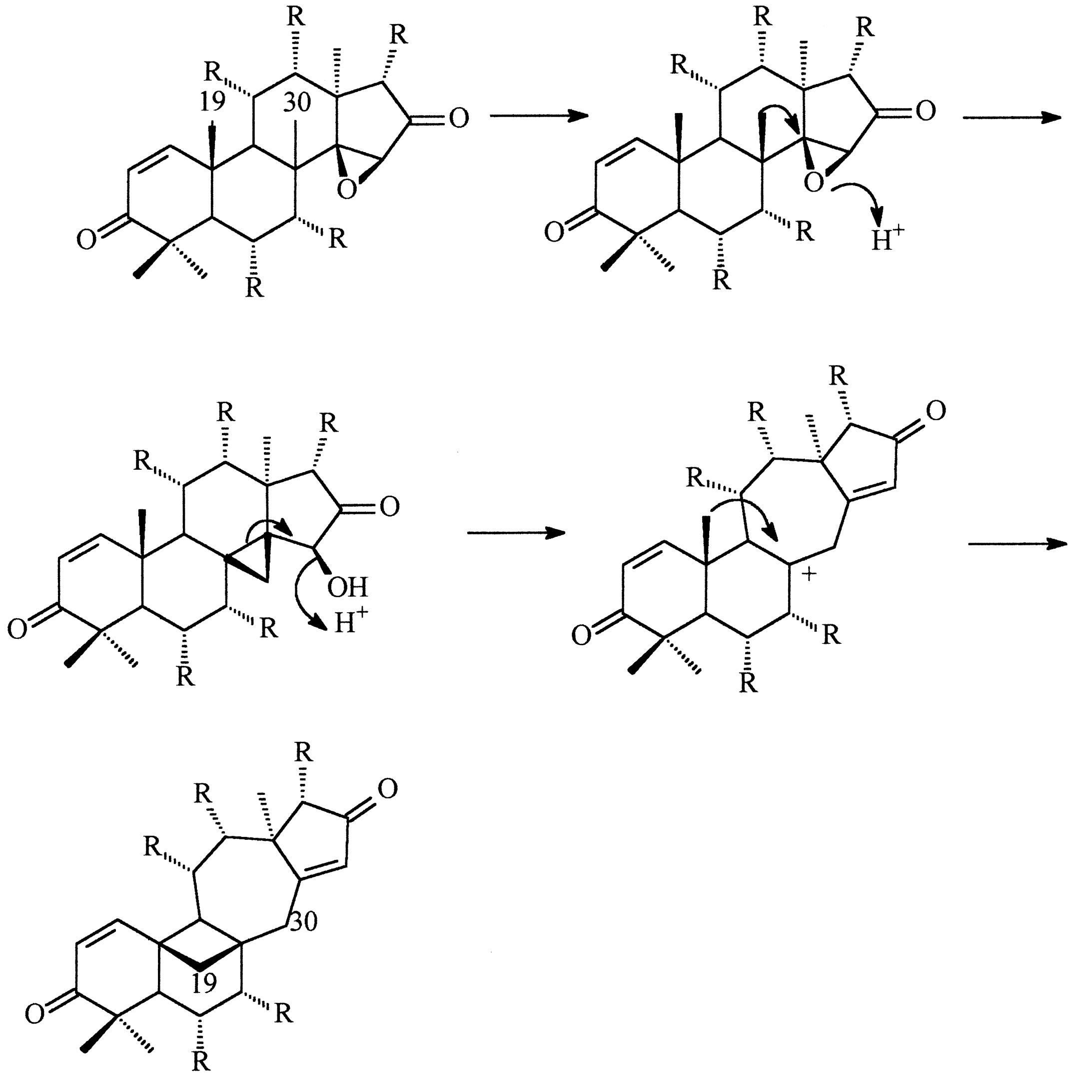
2. Results and discussion

The bark of *E. delevoyi* was milled and extracted with refluxing hexane and yielded the eight compounds described previously (Mulholland et al., 1994) and delevoyin C, after repeated column chromatography. The NMR spectra of delevoyin C, $C_{38}H_{48}O_{13}$, showed it to be related to compounds isolated previously from the same source, having a keto-group at C-16 (δ 205.33) and a 14, 15-double bond in ring D. The ^{1}H-NMR spectrum showed H-15 and H-17 occurring at δ 6.03 and δ 3.29 (d, J = 4.8 Hz), respectively. However, delevoyin C was not a limonoid having a β-substituted five-membered ring lactone at C-17α instead of the limonoid furanyl ring. The C-23 lactonic carbonyl carbon resonance occurred at δ 176.82 in the ^{13}C-NMR spectrum. Furthermore, the ^{1}H-NMR spectrum indicated resonances ascribable to protons of the methyl groups of four acetate and one *iso*-butyrate ester, leaving only three methyl groups instead of the five required for basic limonoid structure. A double bond occurred between C-1 and C-2 with H-1 and H-2 occurring at δ 5.31 and 5.77, respectively. The keto-group which was present at C-3 in 6α-acetoxy-14β,15β-epoxyazadiradione, isolated from the same source, had been converted to an α-acetyl group with H-3 occurring at δ 4.63. The COSY spectrum showed coupling between H-1, H-2 and H-3. Acetoxy groups occurred at C-11α and C-12α and resonances ascribable to H-9, H-11 and H-12 occurred at δ 2.78 (dd, J = 5.4, 10.9), 4.77 [dd, J = 10.9, 8.5] and 4.87 [d, J = 8.5], respectively, in the ^{1}H-NMR spectrum. The fact that H-9 occurred as a double doublet was unusual, and H-9 was seen to be coupled to one of the protons of a methylene group at δ 1.81 in the ^{1}H-NMR spectrum. The HMBC spectrum showed that no



Scheme 1. Proposed biosynthesis of delevoyin C from a precursor such as 14β,15β-epoxy-6α-acetoxyazadirone.

C-19 methyl group was present at C-10. In fact, C-5, C-7, C-9, C-10 and C-8 all showed HMBC correlations with the same methylene group. The other proton of the methylene group occurred as a doublet at δ 1.77 [$J = 11.0$]. This indicated that the C-19 methyl group had been incorporated into a C-8,9,10,19-cycobutanyl ring. The fact that C-8 was incorporated into a cyclobutanyl ring meant that the C-30 methyl group normally present at C-8 had been shifted or modified. The HMBC spectrum showed correlations between C-7, C-8, C-9, C-13, C-14 and C-15 and two protons of another methylene group whose non-equivalent protons occurred at δ 2.49 and δ 2.38 (J = 13.4 Hz). Thus, the C-30 methyl group had been inserted between C-8 and C-14. In Scheme 1, a mechanism for the formation of the cyclobutanyl ring incorporating C-19 and the expansion of ring C to include C-30 is proposed from a precursor such as the co-occurring 6α-acetoxy-14β,15β-epoxyazadiradione. Esters were present at C-6α and C-7α. The HMBC spectrum showed that an acetoxy group was present at C-6α and an isobutyryl group was present at C-7α. The COSY spectrum showed coupling between H-5α, H-6β and H-7β.

Compounds of this type have not been reported previously and use was made of the Logic for Structure Determination (LSD) Program (Nuzillard & Massiot, 1991) to confirm the structure. Structure **1** was the only structure suggested by the program. All ^{1}H- and ^{13}C-NMR resonances could be assigned and are given in Table 1. The stereochemistry at C-3, C-6, C-7 and C-12 could be clearly assigned from the NOESY spectrum. The stereochemistry at C-5, C-9 and C-17 was predicted on biosynthetic grounds and the NOESY spectrum confirmed this. The NOESY spectrum showed a correlation between H-17β, H-12, H-11 and

Table 1
NMR data for delevoyin C (500 MHz, $CDCl_3$, J in Hz)

Atom	^{1}H	^{13}C	HMBC	NOESY
1	5.31*d* (10.0)	133.33	H-2, 3, 5, 19	H-2, 11, 19A
2	5.77*dd* (10.0, 5.9)	124.47	H-1, 3	H-1, 3
3	4.63*d* (5.9)	74.84	H-1, 2, 5, 28, 29	H-2, 28, 29
4	–	36.22	H-2, 3, 5, 6, 28, 29	–
5	2.37*d* (9.3)	45.79	H-1, 3, 6, 7, 9, 19, 28, 29	H-9, 28
6	5.54*dd* (9.3, 6.8)	66.03	H-5, 7	H-19B,28, 29
7	5.50*d* (6.8)	73.57	H-5, 9, 19, 30	H-19B, 30α, 30β
8	–	43.50	H-9, 19, 30	–
9	2.78*dd* (10.9, 5.4)	54.69	H-1, 5, 7, 11, 12, 19, 30	H-5
10	–	40.72	H-1, 2, 5, 19	–
11	4.77*dd* (10.9, 8.5)	65.75	H-9, 12	H-1, 12, 17,19A
12	4.87*d* (8.5)	75.47	H-11, 17, 18	H-17, 18, 20, 30β
13	–	51.37	H-11, 12, 15, 17, 18, 30	–
14	–	175.33	H-15, 18, 30	–
15	6.03*s*	134.31	H-17, 30	H-30β
16	–	205.33	H-15, 17	–
17	3.29*d* (4.8)	52. 38	H-12, 15, 18, 20, 21, 22	H-11, 12, 20, 21, 22
18	1.13*s*	22. 44	H-12, 17, 20	H-12, 20, 21, 22
19A, B	1.77*d* (11.0), 1.81*dd* (11.0, 5.4)	29.69	H-1, 5, 7, 9, 30	H-1, 11; H-6, 7, 29
20	2.70*m*	34.78	H-17, 21, 22	H-11, 12, 17, 18, 21
21	4.44*dd* (8.5, 7.7), 4.41*dd* (8.5, 5.8)	71.95	H-17, 20, 22	H-17, 18, 20, 22
22	2.75*m*	32.11	H-17, 20, 21	H-17, 18, 21
23	–	176.82	H-21, 22	–
28	0.87*s*	20.49	H-3, 5, 29	H-3, 5, 6, 32, 34
29	0.84*s*	24.26	H-3, 28	H-3, 6, 19B
30α, β	2.38*d* (13.4), 2.49*d* (13.4)	33.48	H-7, 15, 19	H-7, 15, 30β; H-7, 12, 30α
31	–	170.48	H-3, 32	–
32	2.06	21.06	–	28
33	–	169.88	H-6, 34	–
34	2.00	20.99	–	28
35	–	176.35	H-7, 36, 37, 38	–
36	2.78*sept* (7.0)	34.46	H-37, 38	
37	1.35*d* (7.0)	19.43	H-36, 38	
38	1.31*d* (7.0)	18.97	H-36, 37	
39	–	170.38	H-11, 40	–
40	1.93	20.41	–	1
41	–	169.56	H-12, 42	–
42	2.11	20.54	–	18, 21

H-19 protons. This indicated that H-11 and H-12 are both β and that delevoyin C is 11α,12α-disubstituted. The stereochemistry at C-20 could not be determined.

3. Experimental

Ground bark (600 g) and wood (1136 g) were extracted separately using a soxhlet apparatus with hexane, chloroform and then methanol. Repeated CC of the hexane extract of the bark extract over silica gel (Merck 9385) yielded six limonoids and two triterpenoids (Mulholland et al., 1994) and delevoyin C. The chloroform extract of the wood yielded gedunin (70 mg) and 11β-hydroxygedunin (70 mg) whose structures were confirmed by comparison of NMR data with literature values (Connolly et al., 1966).

NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. IR spectra were recorded on a Shimadzu-IR spectrophotometer and mass spectra were recorded at the Cape Technikon on a Finnigan 1020 spectrometer.

Delevoyin C (**1**) (20 mg) amorphous, HR MS: M^+ at *m/z* 712.3081 ($C_{38}H_{48}O_{13}$ requires 712.3093), EI MS: 712 $[M]^+$, 653 $[M-CH_3COO]^+$, 695, 522, 462, 402. IR:ν_{max} (NaCl) (cm^{-1}): 3060, 1802, 1755, 1655, 1432, 1297, 1183.

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