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THE STRUCTURE OF ZEYLASTERONE - THE FIRST OF A NEW SERIES OF PHENOLIC 24-NOR-D:A-FRIEDO-OLEANAN TRITERPENES

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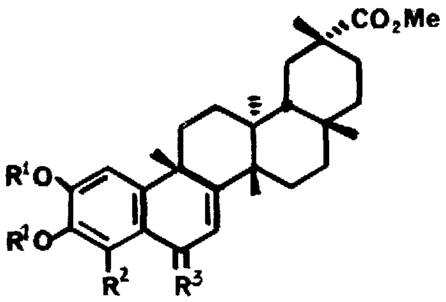
Abstract: Zeylasterone, a new triterpene from Kokoona zeylanica, is shown to be 2,3-dihydroxy-6-oxo-24-nor-D:A-friedo-oleana-1,3,5(10),7-tetraen-23,29-dioic acid-29-methyl ester(20α) (**1**), the first member of a new series of phenolic 24-nor-D:A-friedo-oleanans.

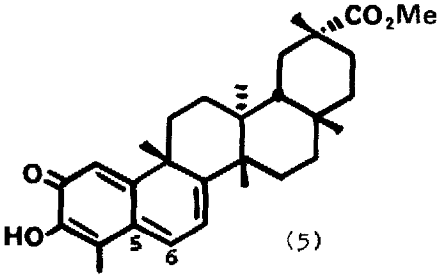
Recently we described the isolation and structural elucidation of eight new D:A-friedo-oleanan triterpenes from the inner bark of Kokoona zeylanica Thw.(Celastraceae).[1-3] We now wish to report the isolation and structure of the first natural phenolic 24-nor-D:A-friedo-oleanan triterpene obtained from the outer bark of the same plant. The structure of this compound which we are naming zeylasterone, is based on the following data.

The light petroleum extract of the outer stem bark of K.zeylanica was separated into neutral, phenolic and acidic fractions. Comparison of the physical data [m.p., i.r. ^1H n.m.r., $(\alpha)_D$ and m.m.p.] of the major compound (0.8% ex. plant material) present in the neutral fraction showed it to be pristimerin (5).[4] Repeated chromatography of the acidic fraction ($NaHCO_3$ soluble) yielded zeylasterone (0.41%) as a colourless crystalline compound, $C_{30}H_{38}O_7$,[5] m.p. 240-242°C, $(\alpha)_D$ -73.4°($CHCl_3$), answering Liebermann Burchard test for triterpenes and $FeCl_3$ test for phenols. Methylation (CH_2N_2) afforded trimethyl zeylasterone (2), $C_{33}H_{44}O_7$, m.p. 229-230°C, $(\alpha)_D$-106.9°($CHCl_3$).

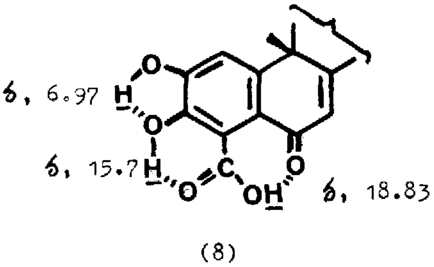
The IR(KBr) spectrum of zeylasterone showed the presence of chelated OH(3502 cm^{-1}), saturated ester carbonyl (1722 cm^{-1}), αβ-unsaturated ketone carbonyl (1642 cm^{-1}) and αβ -unsaturated carboxylic acid (1707 cm^{-1}). In the IR spectrum of the trimethyl zeylasterone the bands due to OH group(s) were absent and the band due to $-CO_2H$ was shifted to αβ-unsaturated ester region (1725 cm^{-1}). The UV spectra of both compounds were comparable with that of 6-oxodimethyl pristimerol (4) further confirming the presence of ArCOC=C- moiety (see Table 1). H_3BO_3-NaOAc induced shift of the UV spectrum of zeylasterone suggested it to contain an ortho-dihydroxy system.[6] Synthesis of (4)



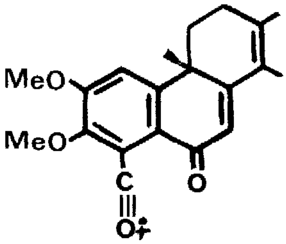
(1) $R^1 = H$; $R^2 = CO_2H$; $R^3 = O$
(2) $R^1 = Me$; $R^2 = CO_2Me$; $R^3 = O$
(3) $R^1 = H$; $R^2 = Me$; $R^3 = O$
(4) $R^1 = R^2 = Me$; $R^3 = O$
(6) $R^1 = H$; $R^2 = Me$; $R^3 = H_2$
(7) $R^1 = R^2 = Me$; $R^3 = H_2$



(5)



(8)



(9); m/e , 325

has been achieved by the sequence; (i) $NaBH_4$ reduction of pristimerin (5) yielding (6),[4] (ii) Me_2SO_4 methylation of (6) giving (7) and finally, (iii) oxidation of (7) with NBS-hν[7] affording (4). IR spectra of (2) and (4) were also found to be superimposable except that in (2) an additional band at 1725 cm^{-1} was present and this was assigned to aromatic ester carbonyl. The base peak at m/e , 325 in the MS of trimethyl zeylasterone (2) was assigned to the fragment (9).[8]

The ^1H NMR spectra (see Table 2) of zeylasterone (1) and its trimethyl derivative (2) were very informative. In the high field region of the spectrum of (1) five 3H singlets due to methyl groups were assigned by comparison with friedelin[9] and pristimerin.[10] The 3H singlet at δ,3.53 was assigned to $-CO_2Me$, and in the low field region the three 1H singlets (exchangeable with D_2O) were assigned to $-CO_2H$ and 2 x OH groups [see (8)]. Further evidence for the assignment of C-1-H, C-7-H, C-20α-CO_2CH_3 and the methyl groups came from the comparison of the spectra of (1) and (2) with that of 6-oxodimethyl pristimerol (4) (See Table 2).

Table 1. UV spectral data of zeylasterone (1), trimethylzeylasterone (2) and 6-oxodimethyl pristimerol (4) in EtOH.

Compound	λ_{max} [log ε] nm				
(1)	211(4.19)	226(4.05)	255(4.08)	295(3.79)	340(3.70)
(2)	207(4.00)	225(3.88)	245(3.99)	287(3.72)	312(3.72)
(4)	210(4.13)	225(4.00)	247(4.07)	285(3.80)	300(3.93)

Table 2. ^{1}H NMR chemical shifts (δ) of zeylasterone (1), trimethyl zeylasterone (2), 6-oxodimethyl pristimerol (4) and pristimerin (5) [60MHz in $CDCl_3$].

Compound	C-1 H	C-7 H	C-4 Me	C-9 Me	C-13 Me	C-14 Me	C-17 Me	C-20β Me	C-4 CO_2Me	C-20α CO_2Me	2,3-di OMe
(1)[a]	6.50	7.33	-	1.60	1.11	1.32	1.17	0.55	-	3.53	-
(2)	6.22	6.95	-	1.60	1.11	1.32	1.17	0.60	3.93	3.53	3.82,3.93
(4)	6.17	6.92	2.70	1.60	1.12	1.32	1.18	0.60	-	3.55	3.78,3.95
(5)[b]			2.20	1.45	1.11	1.27	1.17	0.55	-	3.53	-

[a] For chemical shifts of CO_2H and OH protons, see (8).

[b] Data for protons on C-1, C-6 and C-7 are not indicated.

Table 3. ^{13}C NMR Data of zeylasterone (1) [25.05 MHz in $CDCl_3$].

C	Chemical shift (multiplicity)	C	Chemical shift (multiplicity)	C	Chemical shift (multiplicity)
1	113.8(d)	11	36.2(t)	21	29.8(t)
2	173.7(s)	12	28.6(t)	22	34.4(t)
3	155.5(s)	13	39.7(s)	23	178.7(s)
4	111.3(s)	14	40.5(s)	25	36.8(q)
5	119.4(s)	15	30.9(t)	26	20.2(q)
6	188.0(s)	16	34.8(t)	27	32.7(q)
7	124.4(d)	17	43.0(s)	28	18.3(q)
8	153.4(s)	18	44.2(d)	29	179.8(s)
9	45.6(s)	19	29.8(t)	30	31.6(q)
10	152.8(s)	20	30.5(s)	OCH_3	51.6(q)

The ^{13}C NMR spectrum of zeylasterone (see Table 3) provided additional evidence for the proposed structure (2). Assignment of signals in the aromatic region are based on the published data for acetophenone,[11] flavones[11,12] and xanthones.[13] Alicyclic part of the molecule is assigned by comparison with our data[14] for friedelanones.

Biosynthetically, zeylasterone (1) may be derived from pristimerin (5) (which was found to co-occur in K.zeylanica) by the oxidation of the C-4 Me to C-4-CO_2H and epoxidation of the 5,6-double bond followed by rearrangement to 6-oxo derivative; these transformations taking place in any order, may give rise to zeylasterone (1) .

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