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23-OXO-ISOPRISTIMERIN III: A NEW NATURAL PHENOLIC (9→8)-24-NOR-D:A-FRIEDO-OLEANAN TRITERPENE

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Abstract: The structure of a new natural phenolic (9→8)-24-nor-D:A-friedo-oleanan triterpene isolated from *Kokoona zeylanica* has been established as 23-oxo-isopristimerin III.

Recently we reported the structure of the first phenolic triterpene, zeylasterone, obtained from *K. zeylanica*[1]. We now wish to report a minor triterpene present in this plant whose structure has been established as 23-oxo-isopristimerin III (1), based on the following data.

The IR(KBr) spectrum of 23-oxo-isopristimerin III, $C_{30}H_{38}O_5$[2], m.p. 157-60°, showed the presence of OH (3500-3200(br)cm^{-1}), saturated ester CO (1722 cm^{-1}) and αβ-unsaturated aldehyde CO (1642 cm^{-1}). The UV spectrum (λ max (EtOH,log ε) 263(3.15), 277sh(3.17)) suggested the absence of both pristimerin (6) and zeylasterone type chromophores[1] but indicated the presence of a styrene type chromophore[3]. Further, the H_3BO_3-NaOAc induced UV shift suggested it to contain an ortho-dihydroxy system[4]. Methylation (Me_2SO_4)afforded dimethyl-23-oxo-isopristimerin III (2).

The ^{1}H NMR spectra of (1) (δ 11.93(1H,s,OH), 10.33(1H,s, CHO), 3.53(3H,s, CO_2Me), 1.17 (3H,s, Me) 1.07(6H,s, Me), 0.97(3H,s, Me), 0.80(3H,s, Me) (see also Table) and (2) (δ 10.43 (1H,s, CHO), 3.90 and 3.86(3H each,s, OMe), 3.50(3H,s, CO_2Me), 1.15, 1,05, 1.01, 0.95 and 0.81 (3H each,s, Me), (see also Table) were compatible with the proposed structures and compared well with those of isopristimerin III dimethylether (4)[5] and di-O-acetylisotingenone III (5)[6] (see Table). The base peak corresponding to (10) at m/z 228($C_{14}H_{12}O_3$) formed due to a retro-Diels Alder fragmentation[7] of the M^+ in the high resolution MS of the natural product further supported the proposed structure. It is possible that (1) is an artefact arising due to acid rearrangement of (7). However, the absence of isopristimerin III (3) in the same extract containing pristimerin (6) as the major constituent[1] and the failure of (6) to undergo rearrangement [6,7] under the conditions employed in our isolation procedure rules out the artefactual origin of (1).

Occurrence of (1) in nature is significant as its analogue, isopristimerin III (3) could be the possible biosynthetic precursor of recently encountered novel quinonemethides in nature, pristimerinene (8) and hydroxypristimerinene (9) (see Scheme).

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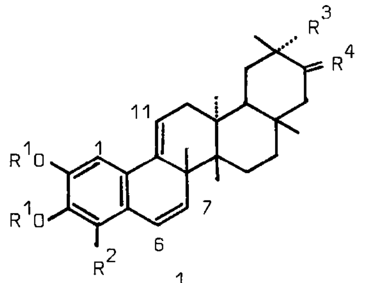


(1) R^1=H; R^2=CHO; R^3=CO_2Me; R^4=H_2

(2) R^1=Me; R^2=CHO; R^3=CO_2Me; R^4=H_2

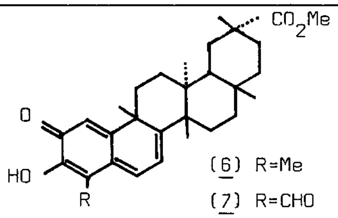
(3) R^1=H; R^2=Me; R^3=CO_2Me; R^4=H_2

(4) R^1=R^2=Me; R^3=CO_2Me; R^4=H_2

(5) R^1=Ac; R^2=Me; R^3=H; R^4=O

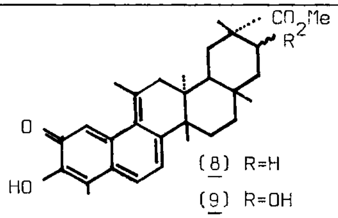
Table. Selected ^1H NMR chemical shifts (δ) of (1), (2) and some related triterpenes.

Structure	C-1H	C-6H, C-7H	C-11H
(1)	7.11 s	7.00 m	5.56 m
(2)	7.00 s	7.15 d, 6.48 d(J=10Hz)	5.57 dd (J=6 and 2Hz)
(4)	6.76 s	6.49 d, 6.30 d(J=8.6Hz)	-
(5)	6.97 s	6.43 q, (J=10Hz)	5.63 dd (J=6 and 2.2Hz)



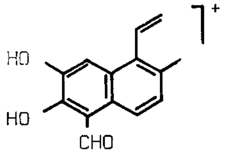
(6) R=Me

(7) R=CHO

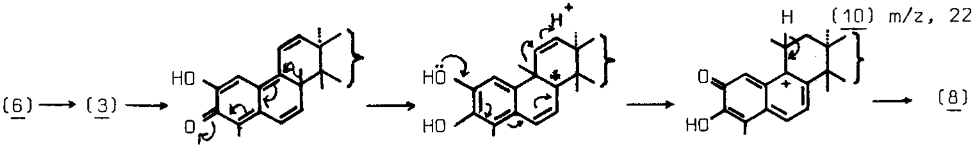


(8) R=H

(9) R=OH



(10) m/z, 228(100%)



Scheme

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