Irradiation of Friedelan-21-ones: Structure Determination of Novel Friedelane Triterpenes from *Kokoona zeylanica*

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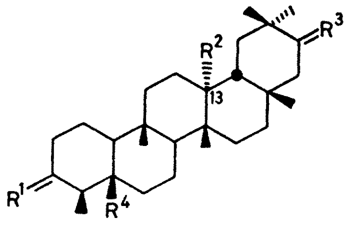
Summary Formation of the photoproducts (**10**) and (**12**) and chemical and spectroscopic evidence suggest that kookononol obtained from *Kokoona zeylanica* is 27-hydroxyfriedelane-3,21-dione (**1**); kokoondiol and kokoonol have been identified as 21α,27-dihydroxyfriedelan-3-one (**2**) and 27-hydroxyfriedelan-3-one (**3**), respectively, by chemical conversions.

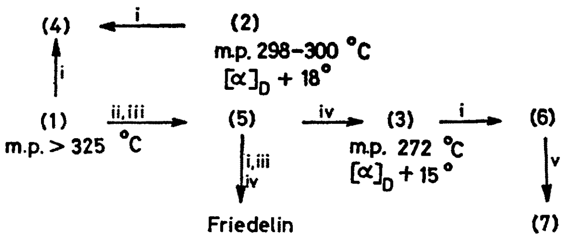
THE value of photolytic cleavage in the location of 21-oxo group in 3β-hydroxyfriedelan-21-one has recently been demonstrated.[1,2] We now report the application of this method to locate the 21-oxo and 27-hydroxy functions in kokoononol, 27-hydroxyfriedelane-3,21-dione (**1**), isolated from the benzene extract of the inner bark of *K. zeylanica* Thw. (Celastraceae). Kokoondiol and kokoonol present in



(1) $R^1 = R^3 = O$, $R^2 = CH_2OH$, $R^4 = Me$
(2) $R^1 = O$, $R^2 = CH_2OH$, $R^3 = \alpha$-OH,β-H, $R^4 = Me$
(3) $R^1 = O$, $R^2 = CH_2OH$, $R^3 = H_2$, $R^4 = Me$
(4) $R^1 = R^3 = O$, $R^2 = CHO$, $R^4 = Me$
(5) $R^1 = [CH_2]_2O_2$, $R^2 = CH_2OH$, $R^3 = H_2$, $R^4 = Me$
(6) $R^1 = O$, $R^2 = CHO$, $R^3 = H_2$, $R^4 = Me$
(7) $R^1 = O$, $R^2 = CO_2H$, $R^3 = H_2$, $R^4 = Me$
(8) $R^1 = \beta$-OH,α-H, $R^2 = CH_2OH$, $R^3 = O$, $R^4 = Me$
(9) $R^1 = O$, $R^2 = Me$, $R^3 = H_2$, $R^4 = CHO$

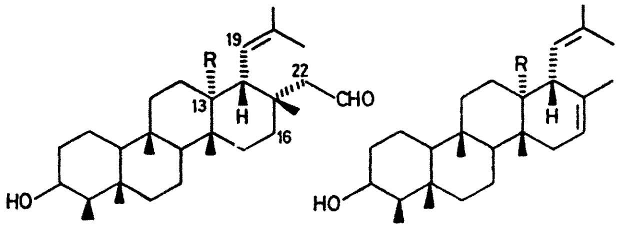
the same extract were shown to be 21α,27-dihydroxyfriedelan-3-one (**2**) and 27-hydroxyfriedelan-3-one (**3**), respectively, by chemical conversions (Scheme 1). Occurrence of friedelanes bearing a hydroxy substituent at C-27 is significant, as of the eight methyl groups in this skeleton it is the most sterically hindered[3] and is the only one which was not encountered previously in nature in an oxidised state.

Spectroscopic evidence suggests that kokoononol† is a friedelane triterpene containing oxo and hydroxymethyl groups [ν 3450 and 1700 cm^{-1}; δ, 4·20 (2H, br s); *m/e* 425 (100%, $M^+ - CH_2OH$)]. The steric crowding around the hydroxymethyl group in kokoonol is apparent from the ^1H n.m.r. spectrum of its acetate which shows a clear dd (*J* 13 Hz) at δ 4·63 and 4·24. Presence of the 3-oxo group was shown by its conversion into friedelin (Scheme 1).



Scheme 1. i, CrO_3, pyridine, 25 °C; ii, $(CH_2OH)_2$, *p*-$MeC_6H_4SO_3H$, C_6H_6, reflux, 8 h; iii, $NH_2NH_2.H_2O$ (98—100%), $(CH_2OH)_2$, 150—160 °C for 5 h, 220 °C for 10 h; iv, *p*-$MeC_6H_4SO_3H$, acetone, reflux, 12 h; v, $KMnO_4$, acetone, reflux, 2 h.

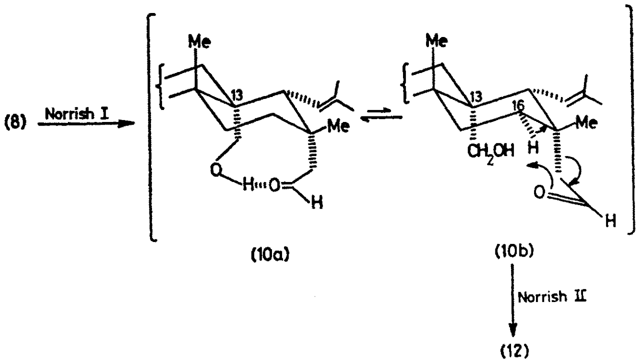
The comparable reactivities of the carbonyl groups of kokoonol in some reactions (acetalisation and $NaBH_4$ and $LiAlH_4$ reductions) to those of friedelane-3,21-dione isolated from the same plant[2] suggested the presence of a second oxo group at C-21. Irradiation (125 W for 12 h, in refluxing dry dioxan) of the $NaBH_4$ reduction product (**8**) of kokoonol proved this to be so.



(10) R = CH_2OH
(11) R = Me

(12) R = CH_2OH
(13) R = Me

The major product (60%) of irradiation is 3β,27-dihydroxy-E-secofriedel-19-ene-21-carbaldehyde (**10**), m.p. 128—130 °C, formed by intramolecular δ-H abstraction within the biradical produced by α-cleavage. The minor product (30%) is 3β,27-dihydroxy-21,22-bisnor-E-secofriedel-16,19-diene (**12**), m.p. 112—114 °C, formed by Norrish type II process from (**10**). Failure to detect the intermediate carbaldehyde (**11**) during the irradiation of 3β-hydroxyfriedelan-21-one under identical conditions suggests a partial inhibition of Norrish type II process on (**10**) which may be possible only if the hydroxymethyl group is present on C-13, avoiding abstraction of 16-H by the $-CH_2CHO$ group (see Scheme 2). ^1H N.m.r. spectrum of (**10**) shows the absence of the hemi-acetal structure. However, the presence of (**10a**) is indicated by the ^1H n.m.r. spectrum of (**10**) which shows significant paramagnetic shifts of the protons (19-H, CH_2OH) in the vicinity of the carbonyl group.



Scheme 2

The attachment of the hydroxymethyl group at C-13 was further confirmed as the oxo-aldehyde (**6**) obtained from kokoonol is different from trichadonal,[3]‡ canophyllal[4]‡ and (**9**),[5]§ and the oxo-acid (**7**) is different from roxburghonic acid,[6]‡ octandronic acid,[7]‡ and polpunonic acid.[8]‡

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† For physical data, see Scheme 1. The composition of all new compounds was confirmed by elemental analysis and high resolution mass spectrometry. Structural assignments are based on i.r. and ^1H n.m.r. spectroscopic evidence.

‡ Direct comparison with an authentic sample.

§ Comparison of physical data (m.p., $[\alpha]_D$, and mass spectrum).

Financial support from the U.S.D.A. and The Chemical Society, London, and a studentship (to N. P. D. N.) from Lever Brothers (Ceylon) Ltd., is gratefully acknowledged. We thank Professor R. H. Thomson for high resolution mass spectra and Professor S. Balasubramaniam for the identification of plant material.

(*Received, 24th November* 1978; *Com.* 1265.)

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