Tetrahedron Letters No. 30, pp 2837 - 2840, 1973. Pergamon Press. Printed in Great Britain.

FOUR NEW FRIEDELANE CARBOXYLIC ACIDS FROM THE BARK OF TRICHADENIA ZEYLANICA THW.(FLACOURTIACEAE)*

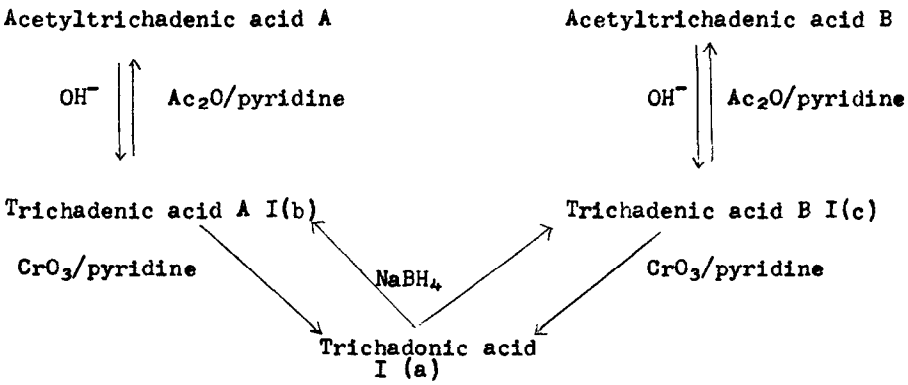
S.P.Gunasekera and M.U.S.Sultanbawa

Department of Chemistry, University of Sri Lanka,

Peradeniya Campus, Peradeniya, Sri Lanka

(Received in UK 31 May 1973; accepted for publication 13 June 1973)

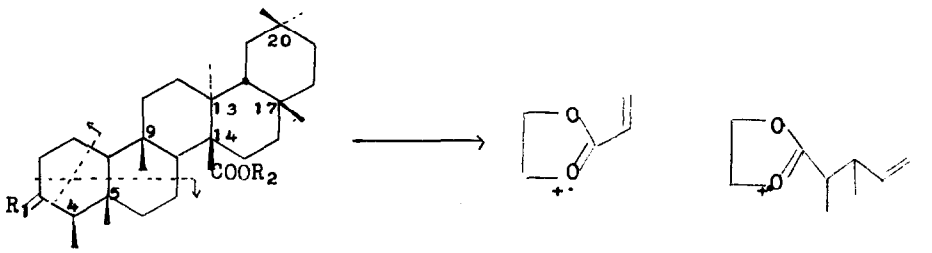
From the light petroleum extract of the bark of the endemic plant, Trichadenia zeylanica Thw., Flacourtiaceae (Sinhala - tolol) four new triterpenoid carboxylic acids, called trichadenic acid A I(b), acetyltrichadenic acid A, acetyl trichadenic acid B and trichadonic acid I(a) have been separated by silica gel chromatography and interrelated as shown below



From the mass spectrum and C,H analysis, trichadonic acid I(a) had a molecular formula $C_{30}H_{48}O_3$. It was saturated and the i.r. spectrum had absorption for a CO group (1716 cm^{-1}) and carboxy group (1685 cm^{-1}). The n.m.r. spectrum showed signals for six tertiary methyl groups and a single secondary methyl group (δ 9.1, J 8Hz), indicating a friedelane skeleton[1]. The methyl ester had an o.r.d. curve similar to friedelan-3-one[2], showing negative Cotton effect having major peak at $(\alpha)_{265}$ + 8460 and a secondary peak at $(\alpha)_{245}$ + 7805 and trough at $(\alpha)_{304}$ - 5946 and a secondary trough at $(\alpha)_{315}$ - 3948. This

indicated that trichadonic acid I(a) was a friedelan-3-one carboxylic acid. The mass spectrum of the ethylene ketal, I(d) of I(a), had the base peak (II) at m/e 99 and the next peak (III) at m/e 153 confirming the 3-position for the keto group and fixing methyl groups at positions 4 and 5.(Scheme I)

Scheme I



I II III

I (a) Trichadonic acid (Friedelan-3-on-26-oic acid), $R_1 = =O$, $R_2 = H$

I(b) Trichadenic acid A (Friedelan-3α-ol-26-oic acid), $R_1 =$  , $R_2 = H$

I(c) Trichadenic acid B (Friedelan-3β-ol-26-oic acid), $R_1 =$  , $R_2 = H$

I(d) Ketal of trichadonic acid, $R_1 =$  , $R_2 = H$

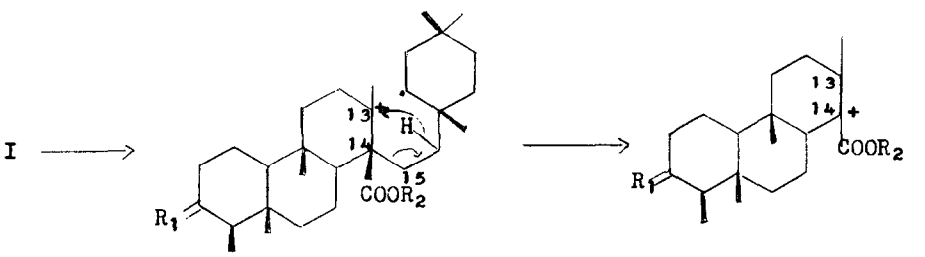
In the n.m.r. spectrum of acetyltrichadenic acid A the proton at the carbon containing the acetyl group had a signal at τ 5.34($W_{1/2}$, 20Hz) whereas in acetyltrichadenic acid B the proton signal was at τ5.11($W_{1/2}$, 5HZ). The different $W_{1/2}$ values established that in trichadenic acid A the 3-OH group was equatorial (α -) and in trichadenic acid B it was axial (β -)[3].

The carboxy group in the compounds I(a), I(b) and I(c) could be at C_9, C_{13}, C_{14}, C_{17} and C_{20} in the friedelane skeleton. Positions C_9 and C_{20} were eliminated for the carboxy group in trichadonic acid I(a) as it was not identical with authentic samples of roxburghonic acid[1], and octandronic acid[4] respectively which had a carboxy group in these positions. Similarly position C_{17} was eliminated in trichadenic acid B I(c) as it was not identical with an authentic sample of

Canophyllic acid[5] which had the CO_2H group at C_{17}. As the mass spectral fragmentation of octandrolic acid[4](friedelan-3β-ol-20β-oic acid) was different from trichadenic acid A, the carboxy group could not have been the C_{20}α-carboxylic acid.

This left only positions C_{13} and C_{14} for the carboxy group. The C_{14} position for the carboxy group is preferred owing to the existence of a fragment (Va) at m/e 305 as base peak in the mass spectrum of trichadonic acid I(a). The formation of V presumably takes place according to the pathway I →IV →V shown below. (If the transfer of proton in IV took place with C_{14} with cleavage of C_{14} - C_{15} bond, the fragment V would have the positive charge in C_{13})[6]. This pathway has been observed in all the related compounds studied as the base peaks V(a)→V(g) are at the appropriate m/e values (See Scheme II)

Scheme II



V(a) from trichadonic acid I(a) at m/e 305

V(b) and (c) from trichadenic acid Acid A and B [I(b) and I(c)] at m/e 307

V(d) from methyl trichadonate [I, R_1= =O, R_2 =Me] at m/e 319

V(e) and (f) from acetyltrichadenic acid A and B [I, R_1 =H, OAc, R_2= H] at m/e 349

V(g) from deoxytrichadonic acid [I, R_1 = H_2, R_2 =H] at m/e 291

This assignment is further supported from steric consideration[6], and is in agreement with the observed reactivity of the carboxy group towards

esterification and hydrolysis reactions. Hence trichadonic acid becomes friedelan-3-on-26-oic acid and trichadenic acids A and B would be friedelan-3α-ol-26-oic acid and friedelan-3β-ol-26-oic acid respectively.

It is hoped to obtain further evidence by X-ray structure determination.

The authors thank Professors W.D.Ollis and R.H.Thomson for spectral data and the National Science Council of Ceylon for a grant. Drs. T.R.Govindachari and C.R.Mitra are thanked for the authentic samples.

REFERENCES

1. H.S.Garg and C.R.Mitra, Phytochemistry, IO ,865(1971)
2. C.Djerassi, R.Rinker and B.Rinker, J.Amer.Chem.Soc., 78, 6362(1956)
3. L.M.Jackman and S.Sternhell, ''Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,'' 2nd Edition, Pergamon, London(1969)
4. S.P.Gunasekera and M.U.S.Sultanbawa, Chem. and Ind.(1973) in the press.
5. T.R.Govindachari, N.Visvanathan, B.R.Pai, U.Ramadas Rao and R.Siriniwasan, Tetrahedron, 23, 1901(1967)
6. cf. T.Kikuchi, M.Niwa and N.Masaki, Tetrahedron Letters, 5249(1972)

* Part V in the series '' Chemical Investigation of Ceylonese Plants''.