Tetrahedron Letters No. 4, pp. 129-134, 1962. Pergamon Press Ltd. Printed in Great Britain.

CHEMISTRY OF TERMINALIA SPECIES - V

POSITION OF THE FOURTH HYDROXYL IN TOMENTOSIC ACID

L. Ramachandra Row and G.S.R. Subba Rao

Department of Chemistry, Andhra University, Waltair

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IN Part I,[1] tomentosic acid was shown to be 2α:3β:23(24):X:tetrahydroxy-olean-12-ene-28-oic acid. The following evidence conclusively places the fourth hydroxyl at the 19th position (I, R = R_1 = H; R_2 = OH).

Triacetyl methyl tomentosate (I, R = Ac; R_1 = Me; R_2 = OH) undergoes smooth oxidation with Cr_2O_3-pyridine to give triacetyl methyl keto tomentosate (II), (λ_{max}^{EtOH} 292 mμ, log ε, 1.92) which gives no phenyl hydrazone and requires forced Wolf-Kishner reduction (Barton's method[2]), suggesting the hindered character of the ketonic group. Further, it does not give rise to a benzylidene derivative[3] indicating the absence of α-methylene group. When refluxed with alkali, an isomeric ketone (m.p. 238-40°; $[\alpha]_D^{28°}$, -13°) (III) was obtained having a strong peak at 248 mμ (log ε, 3.52), characteristic of unsaturated ketones.[4,5] This would point to the migration of the 12(13)-double bond to give α:β unsaturated (13-18) ketone and that is possible only if the ketonic group is in the 19th position.[5] If, therefore, tomentosic acid is 19-hydroxy arjunolic acid (I, R = R_1 = H, R_2 = OH), it should then resemble siaresinolic acid (IV) in the ready elimination of

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[1] L.R. Row and G.S.R.S. Rao, Tetrahedron Letters No. 27, 12 (1960).

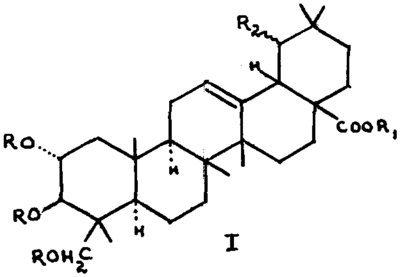
[2] D.H.R. Barton, D.A.J. Ives and B.R. Thomas, J. Chem. Soc. 2056 (1954).

[3] D.H.R. Barton, A.J. Head and P.J. May, J. Chem. Soc. 935 (1957).

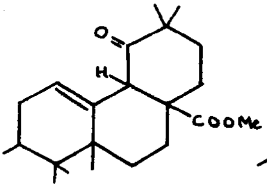
[4] R.B. Woodward, J. Amer. Chem. Soc. 63, 1123 (1941); 64, 76 (1942).

[5] L. Ruzicka, A. Grob, R. Egli and O. Jeger, Helv. Chim. Acta. 26, 1218 (1943).

a molecule of water to give dehydro arjunolic acid (V) with $POCl_3$-pyridine.[6] But triacetyl methyl tomentosate gave rise to anhydro methyl tomentosate (VI) (m.p. 198-200°; $[\alpha]_D^{30^\circ}$, +30°), not identical with methyl dehydro arjunolate[7] (V). However, the dehydration could be successfully accomplished by refluxing triacetyl methyl tomentosate (I, R = AC, R_1 = Me; R_2 = OH) with selenium dioxide for 10 minutes only. Longer periods, usually employed for dehydrogenation (10-20 hr),[7] invariably produced uncrystallizable resins.



I



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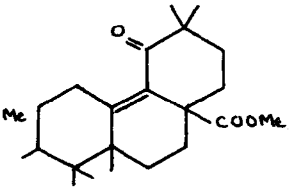

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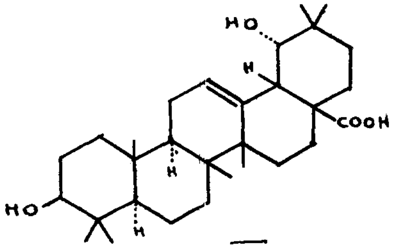

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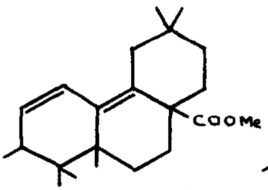

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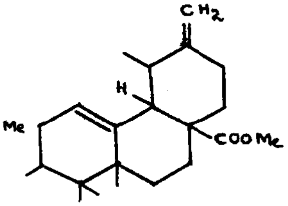

VI

Similar dehydration was also noticed with the pentol tetraacetate (VII, R = AC; R_1 = OH) (m.p. 265-66°; $[\alpha]_D^{30^\circ}$, +42°) obtained by the $LiAlH_4$ reduction of methyl tomentosate (I, R = H, R_1 = Me; R_2 = OH) followed by

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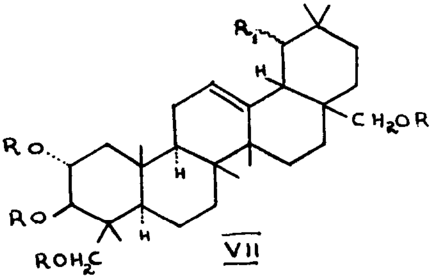
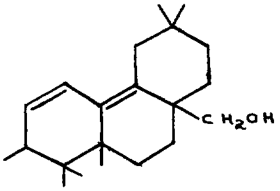
[6] D.H.R. Barton and N.J. Holness, J. Chem. Soc. 78 (1952).

[7] F.E. King, T.J. King and J.M. Ross, J. Chem. Soc. 3995 (1954).

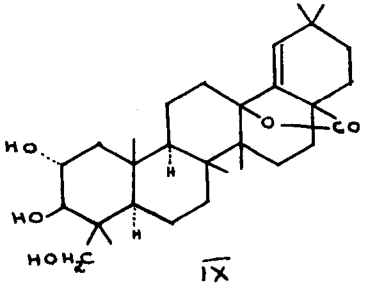
acetylation. The product was identical with dehydro barringtogenol[8] (VIII) (m.p. 282-84°; $[\alpha]_D^{30^\circ}$, -90°) which was secured by the selenium dioxide dehydrogenation of tetracetyl barringtogenol (VII, R_1 = H; R = Ac) (m.p. 265°; $[\alpha]_D^{30^\circ}$, +15°).



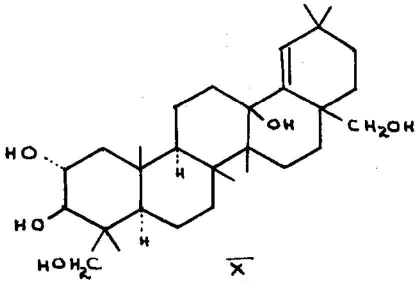
VII



VIII



IX



X

Another reaction which has indirectly supported the 19th position for the fourth hydroxyl is the formation of anhydro lactone (IX) (m.p. 340-42°; $[\alpha]_D^{30^\circ}$, -9°) from tomentosic acid (I, R = R_1 = H; R_2 = OH) with 50% H Br-HAC. This lactone has a trisubstituted double bond; λ_{KBr}, 11.63 μ (860 cm^{-1}) and 12.02 μ (834 cm^{-1}); presumably in 18 (19) position, in view of its marked stability to chromic oxide oxidation.

The conversion of methyl tomentosate to methyl arjunolate has already been reported[1] and this establishes the steric configuration of 18th hydrogen as 18-β-axial hydrogen as in β-amyrin. Ready elimination of

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[8] R. Anantaraman and K.S.M. Pillai, J. Chem. Soc. 4369 (1956).

water to give anhydro lactone (IX) is possible only if it is preceded by the isomerization of 18-β-H to 18-α-H and this is known to happen with HBr-HAC.[6,5] Further, $LiAlH_4$ reduction of the anhydro lactone furnished a hydroxy carbinol (X) (m.p. 280-82°; $[\alpha]_D^{30^\circ}$, $+30^\circ$) different from the carbinol (VII, R = H, R_1 = OH).

The behaviour of anhydro methyl tomentosate (VI) was next studied. It contained an exocyclic double bond (tetranitromethane - yellow) easily reducible with $Pd\text{-}H_2$ under atmospheric pressure. With OsO_4, followed by oxidation with lead tetraacetate, formaldehyde was isolated from anhydromethyl tomentosate (VI), confirming an exocyclic double bond. This is possible only if $POCl_3$ dehydration is accompanied by a Wagner-Meerwin rearrangement of 20-methyl group, with the consequent formation of a double bond as formulated in the accompanying chart (A). It also brings out the

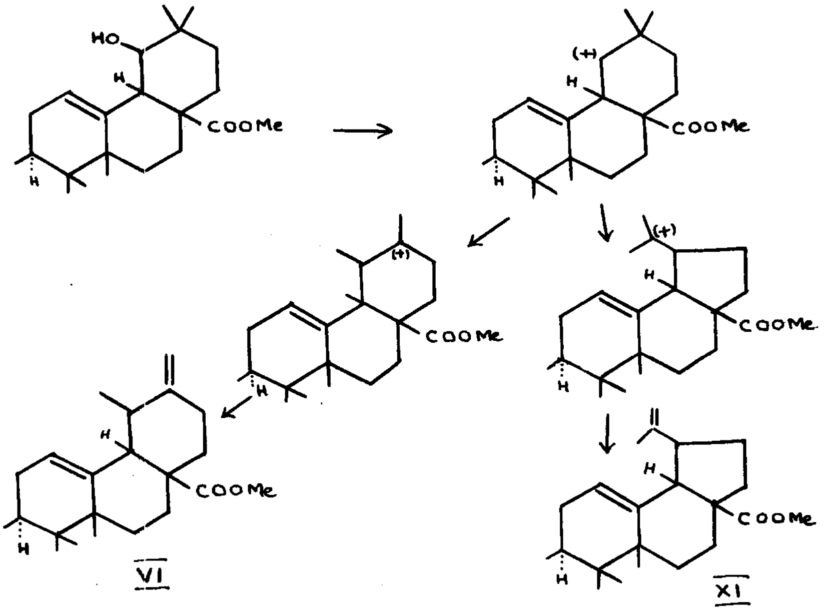
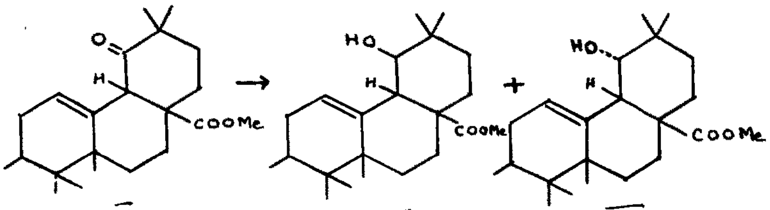


CHART A.

difference between tomentosic and siaresinolic acids. While the latter is 19-α(a)-hydroxy oleanolic acid, the former should have the epimeric configuration of 19-β(e)-hydroxyl which explains the nonformation of methyl dehydro arjunolate with $POCl_3$-pyridine. The alternate possibility of ring contraction to give (XI) is considered remote for the reason that 18(β)H does not favour this course.

In further support of the β-equatorial orientation for the 19th hydroxyl in tomentosic acid, triacetyl methyl keto tomentosate (II) was reduced with sodium borohydride and the carbinol mixture deacetylated and fractionated on alumina. Methyl tomentosate (XIII) and methyl isotomentosate (XII) (m.p. 190-92°; $[\alpha]_D^{30^\circ}$, +43°); were obtained in a proportion of 1:3. Triacetate of the latter suffered dehydration with $POCl_3$-pyridine to give impure methyl dehydro arjunolate (V) recognized by the characteristic triple ultra-violet absorption at 243, 250 and 260 mμ.



II XIII XII

There is only one reported instance with jegosapogenol[9] where dehydration with SeO_2 was complete in 10-15 min. SeO_2 forms a selenous acid ester which obviously under the temperature conditions of the experiment (140°) readily splits off a molecule of selenous acid in cis wise direction (cf. pyrolysis of benzoates[10]) to give rise to 19(18) double bond, which,

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[9] S. Tobinaga, Chem. Abstr. 52, 13686 (1958).

[10] G. Bancroft, Y.M.Y. Haddad and G.H.R. Summers, J. Chem. Soc. 3295 (1961).

being unstable, readily rearranges to 13(18) position.[6]

All the compounds recorded above analysed satisfactorily.

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