THE TRITERPENES OF *CALOTROPIS GIGANTEA* LINN.

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DURING an examination of latex-bearing plants,[1] Asclepiadaceæ were also taken up. Of these, *Calotropis gigantea*[2,3] was examined some time ago in our laboratories. This investigation was started following a remark in the book "The triterpenes", Vol. III, p. 159, by Simonson and Ross that giganteol of Balakrishna, Murthy and Seshadri[3] could be taraxasterol. Also, the authors had suggested further investigation on isogiganteol. In view of our knowledge of other's interest on this plant, we now publish the results of our investigation, and further work on this plant has been abandoned.

The root bark was successively extracted with petroleum ether (b.p. 60–80°), ether and alcohol. Of these, ether and alcohol did not give identifiable compounds, although the former extract contained a mixture of esters (m.p. 160–70°). The petroleum ether extract was examined extensively by chromatography on alumina and fractional crystallisation. After alkaline hydrolysis of the extract, a mixture of the triterpenes were obtained which were separated through their acetates or benzoates. The following were identified: α- and β-amyrins,[4] taraxasterol and its-ψ-isomer[5] and β-sitosterol.[6]

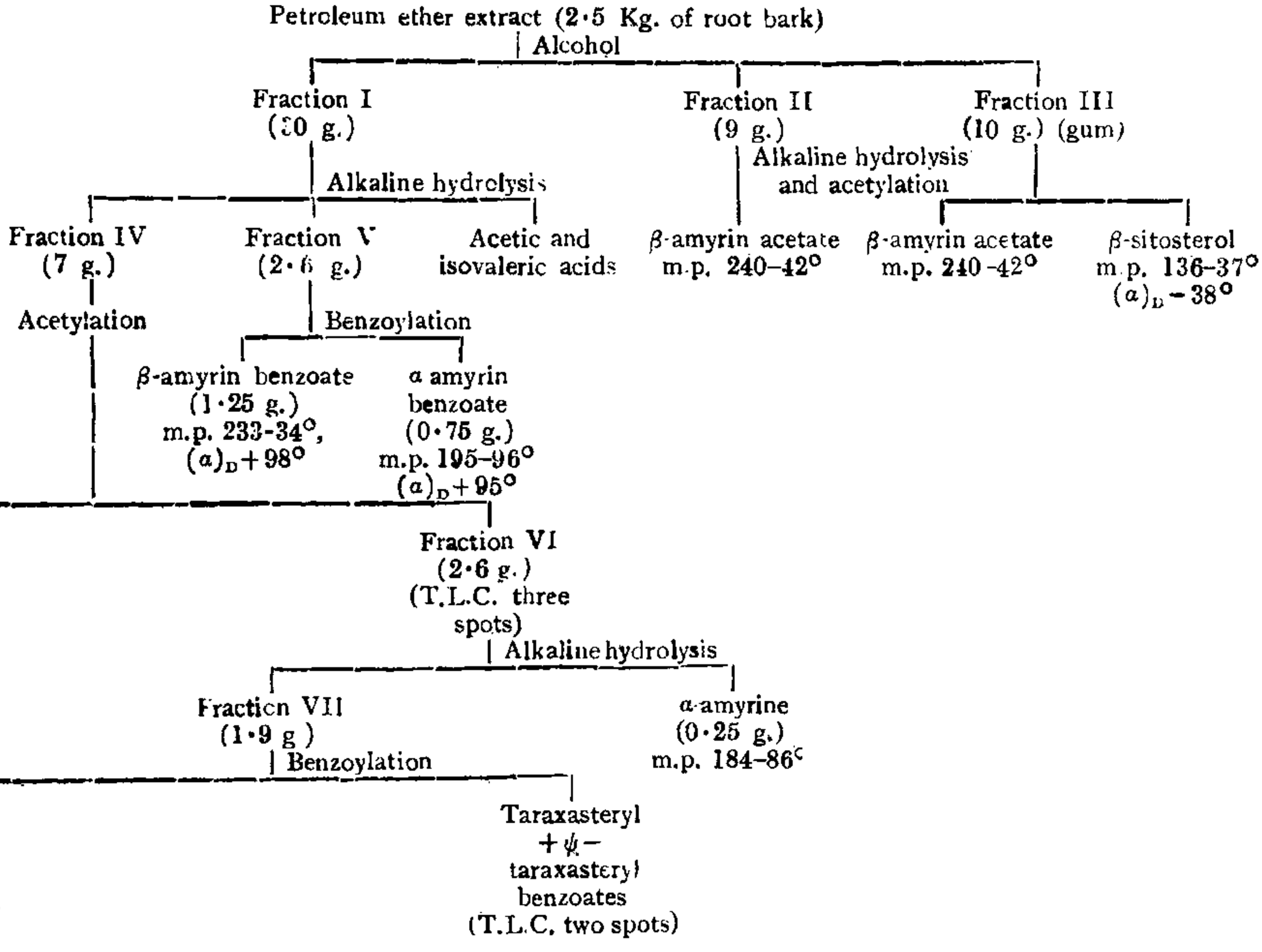
Balakrishna, Murthy and Seshadri[3] recorded the separation of giganteol acetate as first fraction from the acetate mixture and the second fraction as isogianteol acetate. It was recorded that both are monohydric alcohols analysing for $C_{30}H_{50}O_2$; the function of the remaining oxygen being unknown. Following a similar procedure for the fractionation (Chart I) of the mixed acetates, (Fraction IV) using $CHCl_3$-MeOH, the first fraction corresponded closely with giganteol acetate (T.L.C. single spot) of Balakrishna, Murthy and Seshadri,[3] it was identical (m.p. and I.R.) with an authentic sample of taraxasteryl acetate. The second fraction (Fraction VI) showed similar correspondence with that of isogiganteol acetate, but exhibited three prominent spots on T.L.C. Separation of this fraction by further crystallisation from $CHCl_3$-MeOH was not fruitful. It was hydrolysed and fractionated further with $CHCl_3$-MeOH whereby α-amyrin (m.p. 184–86°) could be isolated. The sparingly soluble fraction (Fraction VII) was benzoylated and fractionated to give-ψ-taraxasteryl benzoate, (m.p. 282–83°). The tail fraction contained a mixture of taraxasteryl and ψ-taraxasteryl benzoates (T.L.C., two spots) identified by co-chromatography on T.L.C. In the experiments recorded above, no fraction could be isolated which gave basic analysis of $C_{30}H_{50}O_2$ for alcohols. It was, therefore, presumed that the analysis of Balakrishna, Murthy and Seshadri[3] might be for the hydrates and it is not unknown that taraxasterol crystallised with the solvent of crystallisation.[7]

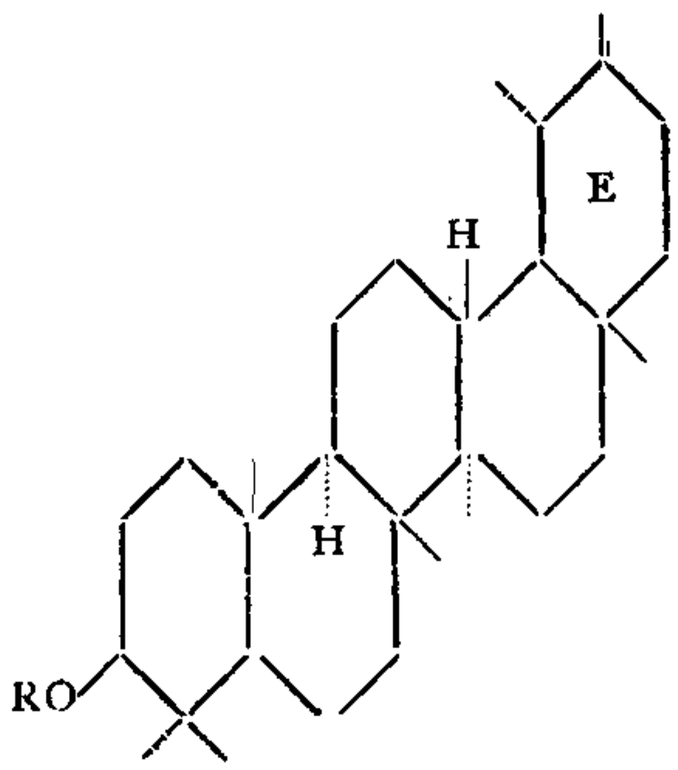
In the hydrolysate of Fraction I (Chart I), acetic acid and isovaleric acid were identified leading to the conclusion that some of the above triterpenes, if not all, might be in the form of their esters. So, unhydrolysed esters were fractionated from alcohol and each fraction chromatographed on alumina column eluting with petroleum ether (b.p. 40–60°), petroleum ether-benzene (1 : 1) and benzene. After several complicated fractionations, β-amyrin acetate, m.p. 240–42°, $(\alpha)_D^{30} + 96°$ and taraxasteryl isovalerate, m.p. 228–29°, were separated from petroleum ether eluate and taraxasteryl acetate, m.p. 254–55°, $(\alpha)_D^{30} + 98°$ from benzene eluate. Three unidentified ester fractions from petroleum ether eluate, m.p. 207–209°, m.p. 195–206° and m.p. 130–40° were not studied any further.

Similar careful extensive fractionation of the petroleum ether extract of the leaves gave rise to β-amyrin, taraxasterol and its ψ-isomer after alkaline hydrolysis. Attempts were made to isolate the esters of these triterpenes. There was good evidence of isovalerate of taraxasterol (m.p. 226–28°); but no attempts were made to confirm.

During the course of identification of taraxasterol (I) through transformation to known compounds, action of protonic reagents was studied. Taraxasterol (I) was reported to be isomerised in presence of 90% formic acid to ψ-taraxasteryl formate (II)[5] and with acetic acid-H_2SO_4 to lupenol-I (III).[8] During our study, it was noticed that $CHCl_3$-HCl readily converts taraxasteryl acetate (IV) to ψ-taraxasteryl acetate (V). The strength of formic acid appears to be crucial, for 80% formic acid in benzene would give the formate

CHART I





I, R=H
IV, R=AC
VI, R=Formyl

II, R=Formyl
V, R=AC

III, R=H
VII, R=AC

ester of taraxasterol (VI) with no isomerisation and similarly HOAc-HCl is a poorer reagent even at 100° than HOAc-H_2SO_4 at room temperature as it yields a mixture of ψ-taraxasteryl acetate and lupenyl-I acetate (VII).

All compounds analysed satisfactorily and they were identified through their derivatives, I.R. spectra and by comparison with authentic samples (M.M.P. and I.R.).

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