Summary

Part-I

Rearrangement of *Taraxa-20α, 30α-Oxido-3β-yl* Acetate With Boron Trifluoride Etherate, Aqueous Perchloric Acid and Dry Hydrogen Chloride.

In the last few decades much attention has been drawn to epoxides in general and a number of organic chemists utilised this three membered epoxide ring as an unique intermediate for the generation of two hetero atoms on the vicinal positions by basic and acidic reagents. The labile nature of this oxide function has made its study quite interesting. The utility and restrictions of various organic and inorganic reagents and selectivity of the solvents have brought to light in the studies of epoxide rearrangements.

The work presented in this part aims at the prediction of plausible mechanisms of formation and establishment of the structures of the rearrangement products obtained by the action of boron trifluoride etherate, aqueous perchloric acid and dry hydrogen chloride on *Taraxa-20α, 30α-Oxido-3β-yl* acetate (II) prepared from Taraxasterol (I). Treatment of the epoxide (II) with BF₃-etherate
in anhydrous benzene for 30 minutes gave two significant products. The less polar one obtained in a variable yield of 15-20\% was a triterpenoid aldehyde acetate, identified as taraxa-30-al-3β-yl acetate (III). The more polar rearrangement product obtained as a keto-acetate (IV) in which ring E has been enlarged giving rise to a seven-membered ring ketone.

Action of aqueous perchloric acid on the epoxide (II), however afforded a keto acetate (V) as the major fraction identified as taraxa-21-one-3β-yl acetate (V) and other products in very small amount.

Treatment of the epoxide (II) with dry hydrogen chloride for 3 hours gave a less polar compound (VI), in a variable yield of 50-60\%, identified as taraxa-30-chloro-20(21)-en-3β-yl acetate and a keto acetate (V), in a variable yield of 15-20\%, identified as taraxa-21-one-3β-yl acetate (V). Another polar compound in low yield was obtained, studies of which is in progress.

The structure of these rearranged products were satisfactorily established on the basis of physical data like IR, PMR, CMR and Mass spectral fragmentation pattern.
Part-II

Chemical Investigation of Salvia Coccinea Linn.

Salvia coccinea Linn is a small tree, annual or sometimes perennial and subshrubby and found in South Canada to Florida, Texas, Mexico, West Indies, Tropical America, cultivated and occasionally escaped in India and Australia. A systematic chemical examination of the petroleum ether extract of the whole plant has resulted in the isolation of a triterpenoid, Triterpene-A (ursolic acid) and β-sitosterol.

Triterpene-A (I), C_{30}H_{48}O_{3}, m.p. 247-249°, ν_{max} 3450 cm^{-1} (-OH gr.), 1690 cm^{-1} (-carbonyl) and 1370 cm^{-1} (gem-dimethyl) responded to diagnostic colour reaction of triterpene. It showed positive tetranitromethane test suggesting the presence of unsaturation in the compound.

On acetylation, Triterpene-A formed a monoacetate (2)
C_{32}H_{50}O_{4}, m.p. 264-268°, [α]_D + 73°, ν_{max} 3280 cm^{-1} (carboxyl-OH gr.), 1730 cm^{-1} (co-stretching), 1370 cm^{-1} (gem-dimethyl) and 1250 cm^{-1} (acetoxy methyl).

PMR spectrum of compound (2) revealed the presence of seven methyl groups (δ 0.65 - 1.00 ppm), one acetoxy group (δ 2.0 ppm), one trisubstituted olefinic hydrogen (unresolved triplet, δ 5.2 ppm),
an axial proton at C-3 (triplet, $\delta$ 4.30 - 4.55 ppm) and methylene protons ($\delta$ 1.5 - 1.8 ppm).

The mass spectral fragmentation pattern of (2) exhibited prominent peaks at m/e 498 ($M^+$), m/e 438, 423, 249, 248 (base-peak), 233, 205, 203, 189 etc. The main fragmentation patterns resembled to that of a pentacyclic triterpenes of $\beta$-amyrine type having -OAc group at C-3.

Compound (2) on methylation furnished the methyl ester (3), $C_{33}H_{52}O_4$ ($M^+$ 512), m.p. 197-198$^\circ$, $[\alpha]_D + 82^\circ$, $\nu_{\text{max}}$ 1720 cm$^{-1}$ (ester carbonyl group), 1250 cm$^{-1}$ (acetoxy methyl) and 1370 cm$^{-1}$ (gem-dimethyl).

The IR spectrum of the compound (3) corresponded to the presence of seven methyl groups ($\delta$ 0.66 - 1.16 ppm), 3 protons (\textsuperscript{6}$\delta$-CH$_3$) at at $\delta$ 2.0 ppm, 1 proton doublet at $\delta$ 2.18 - 2.24 ppm, 1 proton double doublet at $\delta$ 2.78 - 2.88 (due to the protons adjacent to the two secondary methyl groups), ester methyl group (singlet at $\delta$ 3.59 ppm), 1 proton (triplet, $\delta$ 4.4 - 4.58 ppm, $\text{AcO}^-\text{C}-\text{CH}_2$) and 1 proton (illdefined triplet, $\delta$ 5.24 - 5.32 ppm, H-C = CH$_2$). NMR signal at $\delta$ 3.59 ppm affirmed the location of methyl ester function at C-17 position and the signal for one methine proton at $\delta$ 5.24 - 5.32 ppm confirmed the $\Delta^{12}$ position of the double bond.
The mass spectral fragmentation pattern of compound (3) exhibited prominent peaks at m/e 512 (M⁺), m/e 452, 437, 409, 281, 262, 249, 233, 215, 203, 189 etc. The main fragmentation patterns coupled with the presence of peaks at m/e 262, m/e 203 corresponded to that of a pentacyclic triterpenic acid methyl ester having -OAc gr. at C-3. The peak at m/e 203 was characteristic for 28-oic acids (m/e 262-300Me)\(^7\). A Retro-Diels-Alder fragmentation pattern characteristic for \(\Delta^{12}\) pentacyclic triterpenes and a small peak at m/e 249 comprising D and E rings was observed.

All these data along with m.m.p., Co-FIC and superimposable IR spectrum established the identity of the methyl ester of the acetate of Triterpene-A with that of methyl ester of ursa-12-ene-3β-yl-acetate-17-oic acid (3) and hence Triterpene-A was identical with ursa-12-ene-3β-ol-17-oic acid (1).