SUMMARY

The research work being reported in this thesis has been presented in two parts.

Part - I

ACTION OF HYDROGEN PEROXIDE IN PRESENCE OF SELENIUM DIOXIDE ON OXIME DERIVATIVES OF FRIEDELIN; LUPANONE AND TARAXERONE.

Part - I has been divided into three chapters.

CHAPTER - I

This chapter comprises of a concise review of selective oxidation with selenium dioxide and a concise review on reaction of hydrogen peroxide in presence of selenium dioxide.

CHAPTER P II

This chapter contains the action of hydrogen peroxide in presence of selenium dioxide on the oxime derivatives of friedelin : **Section - A;** Lupanone: **Section-B;** and taraxerone; **Section-C**.

Section - A

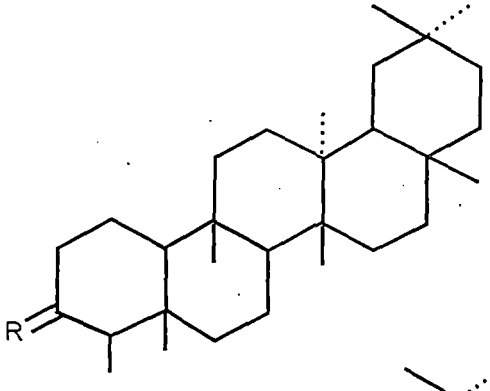
Friedelin oxime **(1)** prepared from friedelin **(1a)** was subjected to oxidation with selenium dioxide containing hydrogen peroxide in tertiary butanol afforded two products; compound A and compound B.

Compound A identified as friedelolactone **(2)**; molecular formula $C_{30}H_{50}O_2$; m.p. 278°C; IR : 1740cm^{-1}; ^{1}H NMR ($CDCl_3$); δ0.82; 0.88; 0.94; 1.00; 1.18; 1.2; 1.22 (7s; 21H; 7 x t-CH_3); δ0.99 (d; 3H; J=6.5Hz; H–C(–CH_3)–); δ2.6 (m;2H;–O–C(=O)–CH_2–CH);δ 4.22 (ABq; 1H; J=6.3Hz; –CO–O–CH –CH_3):

Mass; m/z : 442 (M^+); 427; 398; 383; 274; 245; 219; 218; 206; 205; 191; 177; 163; 149; 123; 109; 107; 95 (base peak).

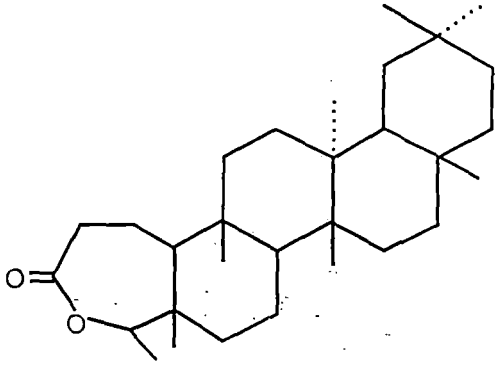
Compound B identified as methyl ester of 2,3-seco-friedelonic acid (**3b**); molecular formula $C_{32}H_{54}O_4$; m.p. 169°–170°C; IR : 1750cm^{-1} (–COOMe);

Mass; m/z : 502(M^+); 487; 471; 455; 442; 429; 415 (base peak); 335; 301; 273; 245; 219; 205 and 191.



1 : R=NOH

1(a) : R=O



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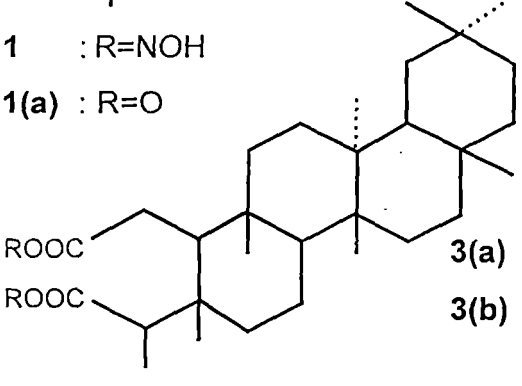


3(a) : R=H

3(b) : R=Me

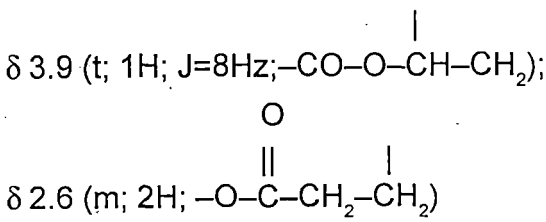
Section - B

Lupanone oxime **(4)** prepared from lupanone **(4a)** was subjected to oxidation with molar proportion of hydrogen peroxide and catalytic amount of selenium dioxide in tertiary butanol afforded two products;compound A and compound B.

Compound A identified as 4, 23, 24-tri-nor-lupan-3 → 5-olide **(5)**; molecular formula; $C_{27}H_{44}O_2$; m.p. 250°–251°C; IR: 1750cm^{-1} (δ-lactone carbonyl group):

Mass : m/z : 400 (m^+); 385; 357, 215, 207, 206, 195, 179, 165, 163, (base peak), 149, 135, 123, 121, 119, 109, 107, 95, 93 and 81 :

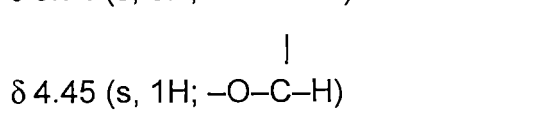
^{1}H NMR ($CDCl_3$): δ 0.75, 0.80; 0.80; 0.87; 0.90; 1.08 (6s;18H; 6 x t–CH_3);
δ 0.75 and 0.80 (2d; 6H; J=7.5Hz; –CH_3);

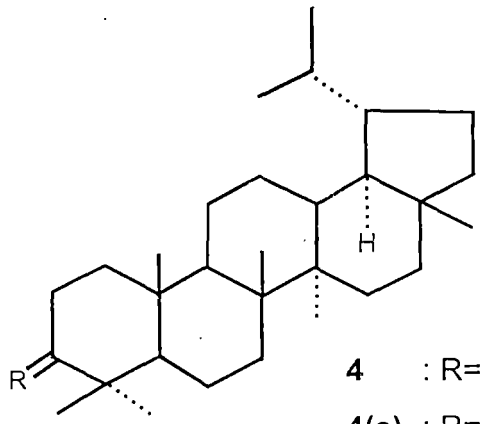


Compound B identified as 1-carbomethoxy – 2, 3–seco-lupan-3→1 olide **(6)**; molecular formula $C_{31}H_{50}O_4$; m.p. 202°–203°C; IR : 1740cm^{-1} (–COOMe) and 1775 cm^{-1} (lactonic carbonyl group);

Mass : m/z : 486 (M^+), 443, 397, 369; 191, 163, 149, 123, 107, 95, 81, 69, 55 (base peak);

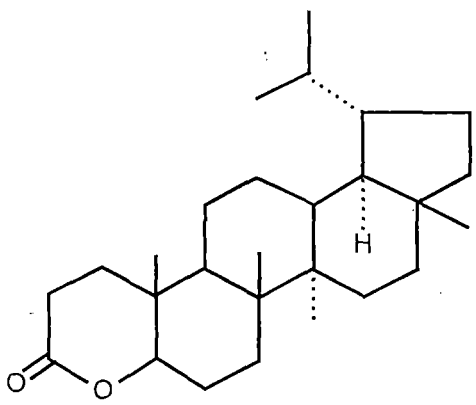
^{1}H NMR ($CDCl_3$): δ 0.76, 0.95,1.11, 1.12, 1.24 and 1.3(6s:18H;6 x t–CH_3)
δ 0.78 (d; 3H; J=6.5Hz; –Me)
δ 0.84 (d; 3H; J=6.5Hz; –Me);
δ 3.74 (s, 3H, –COOMe)





4 : R= NOH

4(a) : R= O



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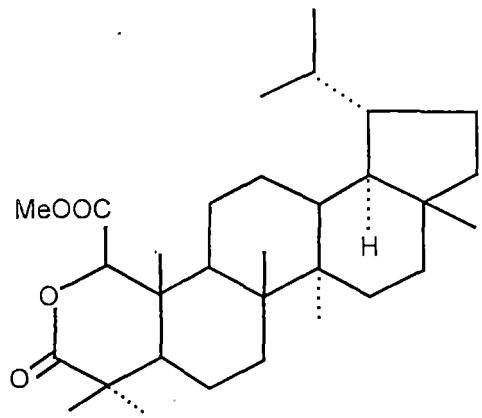


(6)

Section -C

Taraxerone oxime **(7)** prepared from taraxerone **(7a)** was subjected to oxidation with molar proportion of hydrogen peroxide and catalytic amount of selenium-dioxide in tertiary butanol afforded four products: Compound A; Compound B; Compound C and Compound D.

Compound A identified as 4,23,24-tri-nor-taraxerene-3→ 5-αH-olide **(8)**; molecular formula $C_{27}H_{42}O_2$; m.p. 228°–230°C; IR 1750cm^{-1} (δ - lactone carbonyl group) and 810cm^{-1} (tri-substituted double bond);

Mass : m/z : 398 (M^+); 384; 274; 259; 205; 204; 194 and 189.;

^{1}H NMR ($CDCl_3$): δ 0.83 to 1.12 (6s; 18H; 6 x t–CH_3);

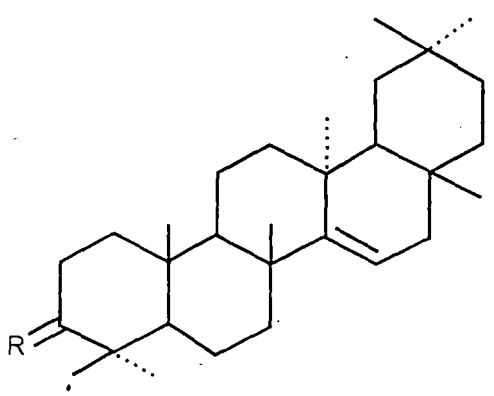
δ 2.26 (m; 2H; –O–C(=O)–$C\underline{H}_2$–CH_2–);

δ 3.92 (q; J_{aa}=12Hz; J_{ae} = 5Hz; 1H ; –COO–$C\underline{H}$–CH_2–);

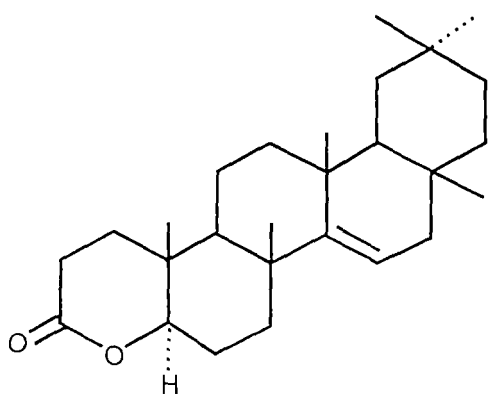
δ 5.57 (m; 1H; $\underline{C}$ = $C\underline{H}$–).

Compound B identified as taraxerene - ε-lactone (**9**); molecular formula $C_{30}H_{48}O_2$; m.p. 218°C; IR: 1720cm^{-1} (ε-lactone carbonyl group) and 810cm^{-1} (tri-substituted double bond):

Mass : m/z : 440(M^+); 425; 316; 301; 205, 204 and 189.



7. R=NOH
7a. R=0



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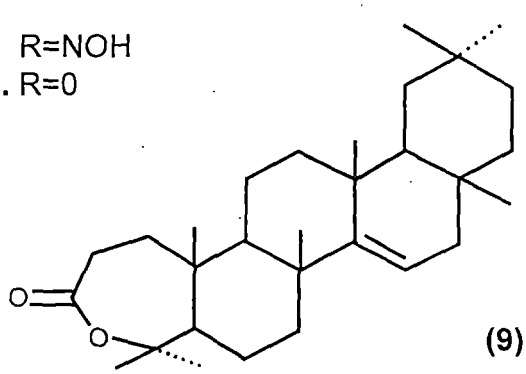

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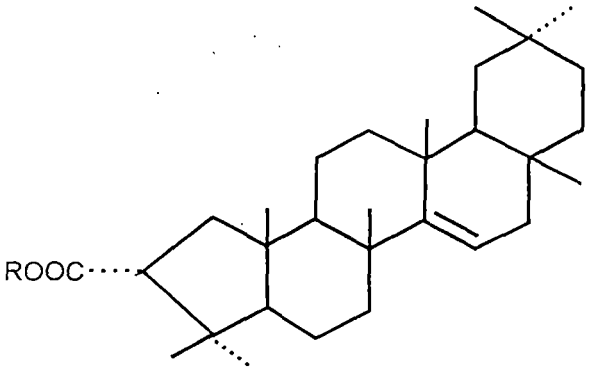
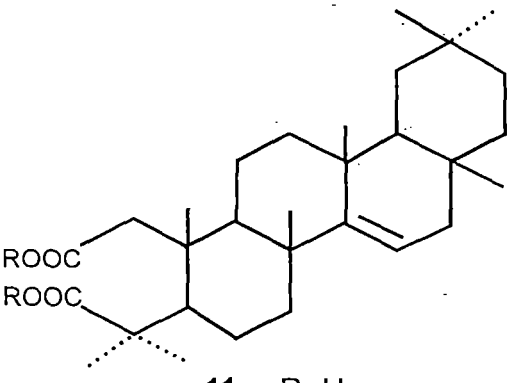
Compounnd C identified as 2α-carbomethoxy-A-nor-taraxerene **(10a)**; molecular formula $C_{31}H_{50}O_2$; m.p. 161°–163°C; IR: 1735cm^{-1} (–COOMe); 1155cm^{-1} (–C–O–stretching vibration of the ester group) and 815cm^{-1} (tri-substituted double bond); mass ; m/z :454 (M^+); 439; 343; 330; 315; 301; 277, 204 and 189; ^{1}H NMR ($CDCl_3$); δ 0.82 to 1.12 (8s; 24H; 8 x t–CH_3): δ 2.75 (q:1H; J_{aa} = 11Hz; J_{ae}= 5Hz; H–C–$COOCH_3$); δ 3.6 (s:3H;–CO–O–CH_3); δ5.54(m; 1H; H–C–CH_2).

Compound D identified as 2,3-seco-methyl taraxerene dicarboxylate **(11a)**; molecular formula $C_{32}H_{52}O_4$; m.p. 151°C; IR: 1730cm^{-1}; 1725cm^{-1} (2 –COOMe); 810cm^{-1} (tri-substituted double bond); mass : m/z 500(M^+); 485; 470; 468; 440; 425; 399; 376; 361; 344; 316; 257; 204 and 189.; ^{1}H NMR ($CDCl_3$); δ 0.81 to 1.25. (8s; 24H; 8 x t – CH_3); δ 2.30 (m; 2H; H_2C–$COOCH_3$); δ 3.60 and 3.65 (2s; 6H.; 2 –$COOCH_3$); δ 5.54 (m; 1H; C=CH–CH_2–).



10 : R=H
10a: R=CH_3



11 : R=H
11a: R=CH_3

CHAPTER - III

This chapter consists of the experimental details of the work described in chapter-II.

PART - II

Action of N-bromosuccinimide in dimethyl sulphoxide on cholest-4-en-3,6-dione.

Part-II has been divided into three chapters.

CHAPTER - I

This chapter comprises of a concise review on the action of N-bromosuccinimide on triterpenoids and steriods.

CHAPTER - II

This chapter contains the action of N-bromosuccinimide in dimethyl sulphoxide on cholest-4-en-3, 6-dione.

A solution of cholest-4-en-3, 6-dione **(I)** dissolved in minimum amount of chloroform was mixed with dimethylsulphoxide (DMSO). N-bromosuccinimide (NBS) was added in excess in small proportions at a time so that the temperature did not rise above 25°C. After the usual work-up the product was obtained. The product so obtained was chromatographed over neutral silica-gel column. The chromatographic separation furnished three compounds : Compound A, Compound B and Compound C.

Compound A identified as 2,7α-dibromo-cholest-1,4-dien-3,6-dione **(II)**; molecular formula $C_{27}H_{38}Br_2O_2$; m.p. 200°–202°C; UV : 259nm: IR :1660cm^{-1} (–$\overset{|}{C}$=C–CO–); CD : 215nm ($\Delta\varepsilon$=9.46), 232.6nm ($\Delta\varepsilon$ =1.6 valley), 240nm ($\Delta\varepsilon$=–0.95), 245.2nm ($\Delta\varepsilon$ = –1.71); 270.8nm ($\Delta\varepsilon$ =5.12) 348.8nm ($\Delta\varepsilon$ =1.26); mass: m/z, 556, 554, 552 (1:2:1) (M^+), 476, 474, 473 (M^+–HBr), 447, 445, 395, 361, 247, 233, 230, 215 (base) 213, 113 (base peak).

PMR; δ 0.77, 1.24 (2s; 2 x t–CH_3); δ 0.85 (d, J=3Hz); δ 0.87 (d, J=3Hz); δ 0.92(d, J=6.5Hz) (3d, 3 x HC–Me); δ 4.41 (d, J = 3.5Hz, H–C–7– Br); δ 6.57 (s; H–C– 4=C); δ 7.45 (s, H–C–1=C).

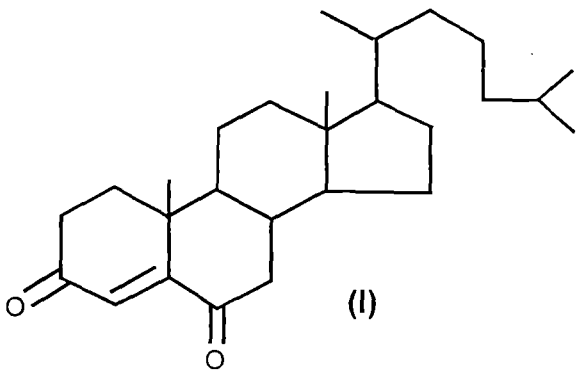
Compound B identified as 2,2,7α-tribromo-cholest-4-en-3,6-dione (III); molecular formula $C_{27}H_{39}Br_3O_2$; m.p. :190°– 191°C,UV : 249nm;IR :1660cm^{-1} (>C=C–CO–); CD : 231nm (Δε=–6.08); 249.8nm (Δε = –3.63 valley); 318.8nm (Δε =1.18); 369.4nm (Δε = – 0.96): mass : m/z : 638, 636, 634, 632 (1:3:3:1) (M^+), 558, 557, 556, 554, 553 (M^+–HBr), 478, 477, 476, 475, 474, 473 (M^+–2HBr), 450, 448, 395. (M^+ –3HBr), 323, 321, 319, 269, 267, 265, 255, 215, 213, 161, 160, 135, 133, 109, 97, 81, 79, 69, 57 (base) :

PMR; δ 0.76, 1.47 (2s, 2 x t–Me); δ 0.86 (d, J=3Hz); δ 0.89 (d, J=3Hz); δ 0.93(d, J=6Hz) (3d, 3 x Sec. – Me); δ 3.28 (ABq, J = 16Hz, 2H, $C\underline{H}_2$);

δ 4.38 (d, 1H, J_{ea} = 3.5Hz, –CO–C(H)(Br)–); δ 6.28 (s, 1H, CO–C=C<u>H</u>)

Compond C identified as 2α,7α – dibromo-cholest-4-en-3,6-dione (IV); molecular formula $C_{27}H_{40}Br_2O_2$; m.p. : 193°–194°C; UV: 249nm; IR;1657cm^{-1} (>C = C – C = O); CD : 214.6nm (Δε = – 2.66, valley) : 219nm (Δε = –3.05); 235.6nm (Δ ε = 4.35); 258.6nm (Δ ε = – 8.87); 351.4nm (Δ ε = – 1.02); mass;m/z 558, 556, 554 (M^+) (1:2:1), 478, 477, 476, 475 (M^+–HBr), 449, 447, 397, 363, 249.

PMR; δ 0.77, 1.24 (2s, 2 x t–Me); δ 0.84, 0.87 (2d, J = 3.5Hz, 2 x Sec –Me); δ 0.94 (d, J = 6.5Hz, 1 x Sec–Me), δ 2.48 (t, 1H, J = 14Hz); δ 2.71 (dd, 1H, J=14Hz); δ 4.86 (dd, 1H, J = 14Hz); δ 4.39 (d, 1H, J = 3.5Hz) and δ 6.34(s,1H).



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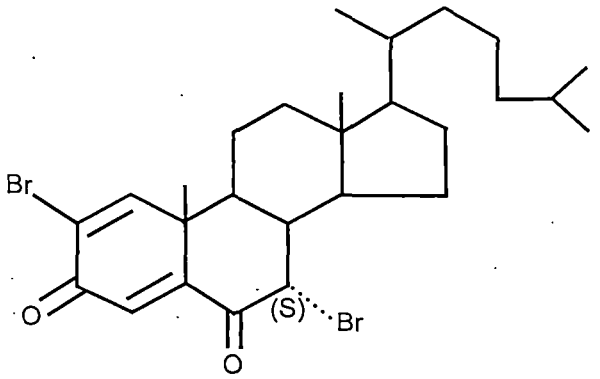

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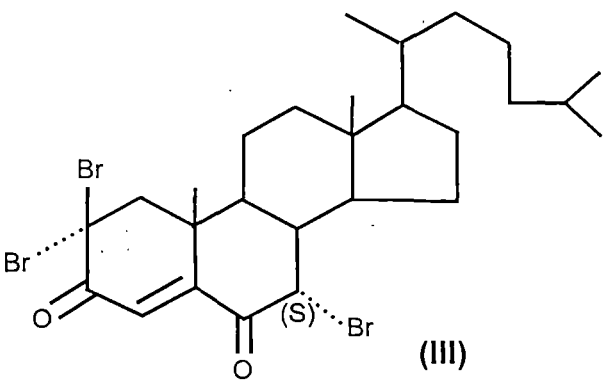

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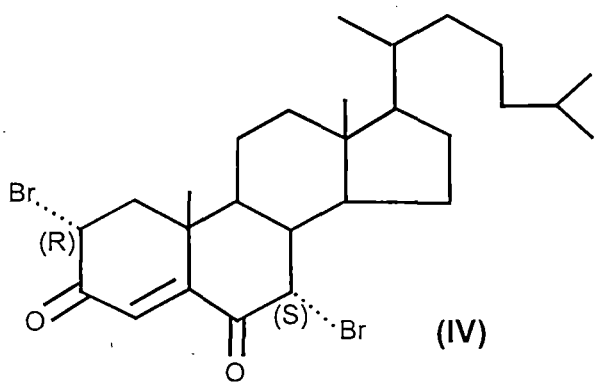

(IV)

CHAPTER - III

This chapter consists of the experimental details of the work described in chapter - II.