

OXIDATION OF FRIEDELIN TO FRIEDELAN 3→4-OLIDE BY *m*-CHLOROPERBENZOIC ACID (*m*-CPBA) IN CHLOROFORM.

0.5 g of friedelin 30 was dissolved in 100 ml.  $\text{CHCl}_3$  and 0.5 g of *m*-CPBA was added. The mixture was then refluxed over waterbath for 6 hours and allowed to cool at room temperature. Then it was diluted with 100 ml. of  $\text{CHCl}_3$  and was washed with 5% of  $\text{Na}_2\text{CO}_3$  solution there by separating into  $\text{CHCl}_3$  and alkali layer. The  $\text{CHCl}_3$  layer was washed with water repeatedly till neutral, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was distilled off yielding a solid mass. It was dissolved in minimum volume of benzene and chromatographed over silica column.

The result of elution with solvents are given below in table-I.

TABLE-I

Eluent	Fraction of 50 ml each.	Residue on distillation.
1. petrol	1-4	nil.
2 petrol-benzene (4:1)	5-9	nil.
3. petrol-benzene (3:2)	10-16	solid (0.4 g)

Further continuation did not afford any more solid.

The fractions 10-16 were crystallised together from  $\text{CHCl}_3$ -MeOH, *M.P.* 271-2°C; identified as 3,4 seco friedelan 3→4-olide 32.

## ANALYSIS REPORT.

Found :	C 80.7 ; H 10.9%
Calculated for $\text{C}_{30}\text{H}_{50}\text{O}_2$ :	C 81.0 ; H 11.0%

IR (Nujol) :  $\nu_{\text{max}}$  1720  $\text{cm}^{-1}$  ( $\alpha$ -lactone)  
fig.1.

Mass : m/e

442 (M<sup>+</sup>), 427, 398, 383,  
274, 245, 218, 205, 123,  
109, 95 (100).

fig.2

<sup>1</sup>H NMR : (CDCl<sub>3</sub>)  
(δ in ppm)

0.82, 0.88, 0.93, 0.98,  
0.99, 1.00 and 1.18.

(7s, 21H, 7X t-CH<sub>3</sub>)

1.20 (d, J=6.5 Hz, CH<sub>3</sub>-C<sub>4</sub>H)

2.60 (m, methylene at C-2)

4.23 (q, J=6.5, C<sub>4</sub>H-CH<sub>3</sub>)

fig.3

TREATMENT OF ALKALI PART :-

The aqueous alkali part was acidified with 20% HCl when a white solid separated out. It was filtered, washed with water and dried. This was found to be m-chlorobenzoic acid by comparing with authentic sample (IR, M.M.P. and Co-tlc)

OXIDATION OF 3-OXO-FRIEDALAN 27 → 15-OLIDE 53 WITH mCPBA :-

0.5 g of 3-oxo-friedelan 27 → 15-olide 53 was dissolved in 100 ml. CHCl<sub>3</sub> and 0.5 g of mCPBA was added. The mixture was refluxed for 6 hours and after workup, the neutral CHCl<sub>3</sub> layer yielded a gummy substance while aqueous alkali part gave only m-chlorobenzoic acid.

The gummy mass was dissolved in minimum volume of benzene and chromatographed. The solvent used are given in table-II below-

TABLE-II

Eluent	Fraction of 50 ml each.	Residue on distillation.
1. petrol	1-4	nil.

2	petrol-benzene (4:1)	5-9	nil.
3.	petrol-benzene (3:2)	10-14	nil.
4.	petrol-benzene (1:4)	15-20	solid.

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 The fraction 15-20 were combined and crystallised from  $\text{CHCl}_3$ -MeOH,  $M.P. > 300^\circ\text{C}$ ; identified as friedelan 3 $\rightarrow$ 4,27 $\rightarrow$ 15 di-olide 54.

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**ANALYSIS REPORT.**  
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Found :	C 76.01 ; H 9.15%
Calculated for $\text{C}_{30}\text{H}_{46}\text{O}_4$ :	C 76.59 ; H 9.70%

IR (Nujol) : $\nu_{\text{max}}$	1730 and 1760 $\text{cm}^{-1}$ (C=O of $\epsilon$ and $\gamma$ -lactone moiety.)
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fig.4

Mass : m/e	470 ( $M^+$ ), 426, 408, 383, 363, 123 (100).
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fig.5

$^1\text{H}$ NMR : ( $\text{CDCl}_3$ ) ( $\delta$ in ppm)	0.85, 0.90, 0.95, 0.96, 1.00 and 1.16 (6s, 18H, 6X t- $\text{CH}_3$ ) 1.20 (d, J=6.5 Hz, $\text{CH}_3$ - $\text{C}_4\text{H}$ ) 2.46 (m, 1H, 2 $\alpha$ -H) 2.63 (m, 1H, 2 $\beta$ -H) 4.19 (q, $\text{CH}_3$ - $\text{C}_4\text{H}$ ) 4.35 (t, J=3 Hz, 15 $\beta$ -H)
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fig.6

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**OXIDATION OF ACETYL METHYL BETULINATE 56 WITH m-CPBA IN  $\text{CHCl}_3$ .**  
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1.0 g of acetyl methyl betulinate 56 was dissolved in 100 ml.  $\text{CHCl}_3$  and 1.0 g of m-CPBA was added. The mixture was than refluxed for

6 hours and allowed to cool at room temperature. After usual workup, the neutral  $\text{CHCl}_3$  layer yielded a gummy white mass while the alkali layer gave m-chlorobenzoic acid.

The gummy mass which showed to distinct spots on tlc plates was dissolved in minimum benzene and chromatographed over silica gel. The results are given in the table-III below-

TABLE-III  
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Eluent	Fraction of 50 ml each.	Residue on distillation.
1. petrol	1-4	nil.
2. petrol-benzene (4:1)	5-8	nil.
3. petrol-benzene (3:2)	9-12	nil.
4. petrol-benzene (2:3)	13-15	nil.
5. petrol-benzene (1:4)	16-20	solid. (0.2 g)
6. benzene	21-24	nil.
7. benzene-chloroform (4:1)	25-30	solid. (0.35 g)

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Further elution did not afford any more solid.

Fractions 16-20 were crystallised together from  $\text{CHCl}_3$ -MeOH, M.P.  $151-2^\circ\text{C}$ ; identified as lupan 20-formate, 28-carbomethoxy  $3\beta$ -yl acetate 57.

ANALYSIS REPORT  
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Found :	C 72.10 ; H 10.41%
Calculated for $\text{C}_{33}\text{H}_{54}\text{O}_6$ :	C 72.24 ; H 10.72%

IR (Nujol) :  $\nu_{\max}$  1740 and 1250  $\text{cm}^{-1}$   
 (-COOCH<sub>3</sub> and -O-COCH<sub>3</sub>)  
 fig.7.

Mass : m/e 544 (M<sup>+</sup>), 498, 484, 438,  
 423, 410, 395, 379, 249,  
 189 (100).  
 fig.8.

<sup>1</sup>H NMR : (CDCl<sub>3</sub>) 0.80-0.96 (5s, 15H, 5X t-Me), 3.65 (s, 3H, -COOCH<sub>3</sub>)  
 ( $\delta$  in ppm.) 1.2 (dd, J=7 Hz, -CH-CH<sub>3</sub>), 4.67 (m, 1H, C<sub>3</sub>- $\alpha$ H)  
 2.04 (s, 3H, -OCOCH<sub>3</sub>), 7.99 and 8.12  
 (ss, 1H, -O-CHO).

fig.9

Similarly, fractions 25-30 were collected and crystallised from CHCl<sub>3</sub>-MeOH, *M.P.* 211-2<sup>o</sup>C; it was identified as 29-nor-acetyl methyl 20-oxo-betulinic acid 58.

ANALYSIS REPORT.

Found : C 74.30 ; H 10.21%  
 Calculated for C<sub>32</sub>H<sub>50</sub>O<sub>5</sub> : C 74.70 ; H 10.50%

IR (Nujol) :  $\nu_{\max}$  1730 (broad) and 1260  $\text{cm}^{-1}$   
 (-COCH<sub>3</sub>, -OCOCH<sub>3</sub> & -COOCH<sub>3</sub>)  
 fig.10.

Mass : m/e 514 (M<sup>+</sup>), 454, 439, 411,  
 395, 372, 237, 190,  
 189 (100)  
 fig.11.

<sup>1</sup>H NMR : (CDCl<sub>3</sub>) 0.83, 0.84, 0.89, and 0.99, 3.2-3.3 (ddd, 1H, J=4 Hz,  
 ( $\delta$  in ppm) (4s, 9H+6H, 5X t-CH<sub>3</sub>) -C<sub>19</sub>-H)  
 2.03 and 2.17 3.67 (s, 3H, -COOCH<sub>3</sub>)  
 (2s, -COCH<sub>3</sub>, -OCOCH<sub>3</sub>) 4.46 (m, 1H, -C<sub>3</sub>- $\alpha$ H)  
 2.25 (t, 1H, J=3 Hz, -CH-)

fig.12.

REFERENCES.

1. H.Hibbert and P.Burt, Org.Syn.Coll.1, 494, (1944).
2. H.B.Henbest and R.A.L.Wilson, J.Chem.Soc. 3289, (1956).
3. M.S.Ahmad et al, Tetrahedron, Vol.36, 16, (1980).
4. B.Rickborn and S.Y.Lwo, J.Org.Chem. 30, 2212, (1965).
5. R.Adams, V.Voorhees and R.L.Shriner, Org.Syn.Coll.Vol.1, 463, (1944).
6. R.H.White and W.D.Emmons, Tetrahedron, 17, 31, (1962).
7. W.D.Emmons, A.S.Pagano and J.P.Freeman, J.Am.Chem.Soc. 76, 3472, (1954).
- 8a. B.M.Lynch and K.H.Pausacker, J.Chem.Soc. 1525, (1955).
- b. R.Kaveic and B.Plesnicar, J.Org.Chem. 35, 2033, (1970).
- 9a. H.Kwart, P.S.Starcher and S.W.Tinslay, Chem.Comm. 7, 335, (1967).
- b. A.Azman, B.Borstnik and B.Plesnicar, J.Org.Chem. 34, 971, (19669).
- 10a. C.H.Hassal, Org.Reactions, 9, 73, (1957).
- b. P.A.S.Smith in P.deMayo ed., Molecular rearrangement, Vol.I  
Wiley-Inter Sc. New York, 568-91, (1963).
11. W.D.Emmons and G.B.Lucas, J.Am.Chem.Soc. 77, 2287, (1965).
- 12a. W.Von E.Doering and L.Speers, J.Am.Chem.Soc. 72, 5515, (1950).
- b. Y.Ogata and Y.Sawaki, J.Org.Chem. 34, 3985, (1969).
- 13a. S.L.Friess, J.Am.Chem.Soc. 71, 2571, (1949).
- b. S.L.Friess and P.E.Frankenburg, J.Am.Chem.Soc. 74, 2679, (1952).
- c. J.L.Mateos and H.Menchaca, J.Org.Chem. 29, 2026, (1964).
14. W.F.Sager and A.Duckworth, J.A.C.S. 77, 188, (1955).

- 15a. M.F.Hawthorne and W.D.Emmons, J.A.C.S. 80, 6398, (1958).
- 15b. E.E.Smissman, J.P.Li and Z.N.Isvaili, J.Org.Chem. 33, 4231, (1968)
- c. A.Nishihara and I.Kubota, J.Org.Chem. 33, 2525, (1968).
- d. R.D.Chambers and M.Clark, Tetrahedron Letters, 32, 2741, (1970).
- 16a. W.Von E Doering and E.Dorfman, J.A.C.S., 75, 5595, (1953).
- b. S.L.Friess and N.Franham, J.A.C.S. 72, 5518, (1950).
- c. S.L.Friess and A.H.Sholoway, J.A.C.S. 73, 3968, (1951).
- d. S.L.Friess and R.Pinson, J.A.C.S. 74, 1302, (1952)
- e. B.W.Palmer and A.Fry, J.A.C.S. 92, 2580, (1970).
- f. R.R.Sauers and R.W.Ubersax, J.Org.Chem. 30, 3939, (1965).
- g. J.C.Robertson and A.Swelim, Tetrahedron Letters, 30, 2871, (1967).
- 17a. R.B.Turner, J.A.C.S. 72, 878, (1950)
- b. T.F.Gallagher and T.H.Kritchevsky, J.A.C.S. 72, 882, (1950).
- c. K.Mislow and J.Brenner, J.A.C.S. 75, 2318, (1953).
- d. J.A.Berson and S.Suzuki, J.A.C.S. 81, 4088, (1959).
- e. J.D.McClure and P.H.Williams, J.Org.Chem. 27, 24, (1962).
- 18a. R.R.Sauers, J.A.C.S. 81, 925, (1959).
- b. R.R.Sauers and G.P.Ahearn, J.A.C.S. 83, 2759, (1961)
19. Fumio Toda, M.Yagi and K.Kiyoshige, J.Chem.Soc. Chem.Comm. 14, 958, (1988).
20. S.Hara, N.Matsumoto and M.Takenchi, Chem. and Ind. 2086, (1962).
21. V.Prelog, L.Ruzicka, P.Meister and P.Wielend, Helv.Chem.Acta. 28, p-618, p-1651, (1945).

22. G.H.Whittam, J.Chem.Soc. 2016, (1960).
23. T.Hase, Chem.Comm. 755, (1972).
24. M.Tori, R.Matsuda, M.Sono, Y.Kohama and Y.Asakawa, Bull.Chem.Soc. Japan, 61, 2103-8, (1988).
25. C.P.Dutta, U.K.Som and K.P.Dhara, Ind.J.Chem.Soc. Vol. LXV, 8, 604, (1988).
26. C.P.Dutta, J.Banerjee, G.Dutta, U.K.Som and K.E.Haque, Ind.J.Chem.Soc. 67, 10, 842, (1990).
27. A.Patra and S.K.Chowdhury, Ind.J.Chem. 27B, 170, (1988).
28. I.Agata, E.J.Corey, A.G.Hortmann, J.Klein, S.Proskow, and J.J.Ursprung, J.Org.Chem. 30, 1698, (1965).
29. B.P.Pradhan, S.K.Chakraborty and P.Meyerstahl, Tetrahedron Letters 30, 5463, (1989).
30. J.Simonsen and W.C.J.Ross, The Terpenes, Vol.IV, Cambridge Univ. Press, Cambridge, (1957).