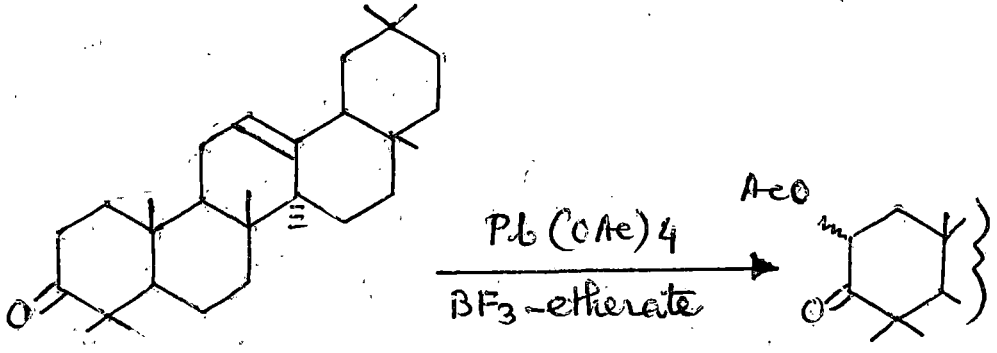
CHAPTER - II

Studies on autoxidation : Unambiguious synthesis of methyl dihydro-alphitolate (section B) and 2β, 3β-dihydroxy betulinate (section C) from betulinic acid.

Section A : Introduction :

During the course of studies on autoxidation in β - amyrone series Khastgir et al[106] found that the 2α-acetoxy-β-amyrone 29 (page 92) obtained by acetylation of diosphenol 27 and subsequent hydrogenation of the diosphenol acetate differed from that of the 2α-acetoxy-β-amyrone 145 obtained by direct acetoxylation of β-amyrone 26 by lead tetra acetate in presence of BF_3 - etherate in benzene solution. Acetoxylation at the α-position to

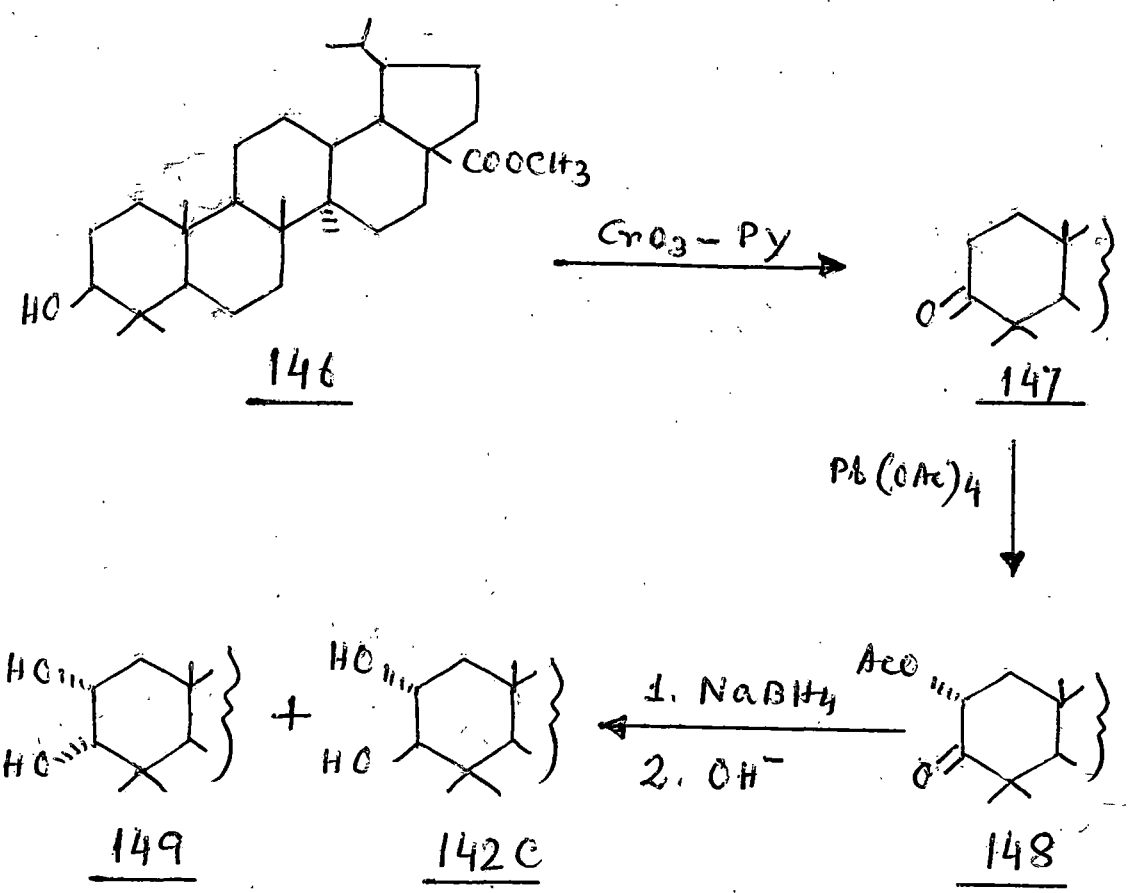


26 145

the 3 - keto group in ring A of triterpenoids with lead tetraacetate leading to 2α-acetoxy-3-keto compounds is well documented [18,57,58]. This reaction, thought to proceed via the enol[22] is expected to yield a product resulting by attack from the less hindered α - side. They reported the isolation of an acetoxy ketone 145 having the same melting point and m.m.p. 158 - 60° as 29 prepared by hydrogenation of diosphenol acetate but their IR spectra revealed significant deviations in the region 1225 - 1245 cm^{-1} and 1070 - 1095 cm^{-1}. This observation led them to believe that most probably the lead tetraacetate acetoxylation product 145 could be a mixture of conformational isomers. Relevent to this observation is the paper of Jones et al[59] in which they stated that acetoxylation of 3-keto triterpenoids can cause conformational changes in ring A. Khastgir et al[60] also studied the NMR spectra of the two compounds 29 and 145 and they concluded that the lead tetraacetate acetoxylation product 145 was a mixture of conformational isomers. The NMR spectrum of the compound 29 showed a multiplet at 5.62 ppm for the proton at C - 2[39]. As the X part of an ABX pattern with a width of 20 Hz (sum of J) the proton must be axial with an axial-axial and an axial-equatorial coupling. Thus the acetoxy group at C - 2 in 29 is equatorial and predominantly contained one isomer. However, the NMR spectrum

of 145, showed a doubling of several signals. The region of peaks associated with C - 2 proton in 145 was complex and showed several additional peaks. From these observations they stated that 145 must be a mixture of isomers.

Furthermore, Row and co-workers[61] attempted the synthesis of methyl dihydroalphitolate 142 C starting from methyl dihydrobetulinate 146 according to the following scheme:



146 147 149 142C 148

The compound 146 was prepared by catalytic reduction of methyl betulinate in ethanol using Raney nickel-hydrogen at 100°/400 lb. or Adams' catalyst. Oxidation of 146 with chromium trioxide - pyridine furnished 3-keto methylester 147 as colourless plates, m.p. 203-5°, $(\alpha)_D^{30^\circ}$ + 9° which was subjected to acetoxylation with lead tetraacetate under varying conditions and the best yield of 2α-acetoxy-3-keto ester 148, m.p. 215-16°, $(\alpha)_D^{30^\circ}$ + 4°, ν_{max} 1735 and 1720 cm^{-1} was obtained when 3-keto ester 147 was heated at 100° with freshly prepared lead tetraacetate in glacial acetic acid. Reduction of 148 with sodium borohydride followed by mild alkaline hydrolysis gave a mixture of glycols (142 C and 149) which was separated by chromatography on alumina. The minor fraction was found to be a mixture of and the major fraction crystallised from methanol as colourless needles, m.p. 228-30°, $(\alpha)_D^{30^\circ}$ + 1.2°, ν_{max} 3600, 1720 cm^{-1}. It consumed 1.15 moles of lead tetraacetate within 8-hr indicating the presence of a trans-1,2 - glycol system. It was therefore, regarded to be methyl 2α, 3β-dihydroxy-lupan-28-carboxylate 142 C . Row et al[61] reported that the compound 142 C showed no depression of in melting point on admixture with an authentic sample but the IR comparison showed a significant difference. This is in accord with the observations stated by Khastgir et al[10a].

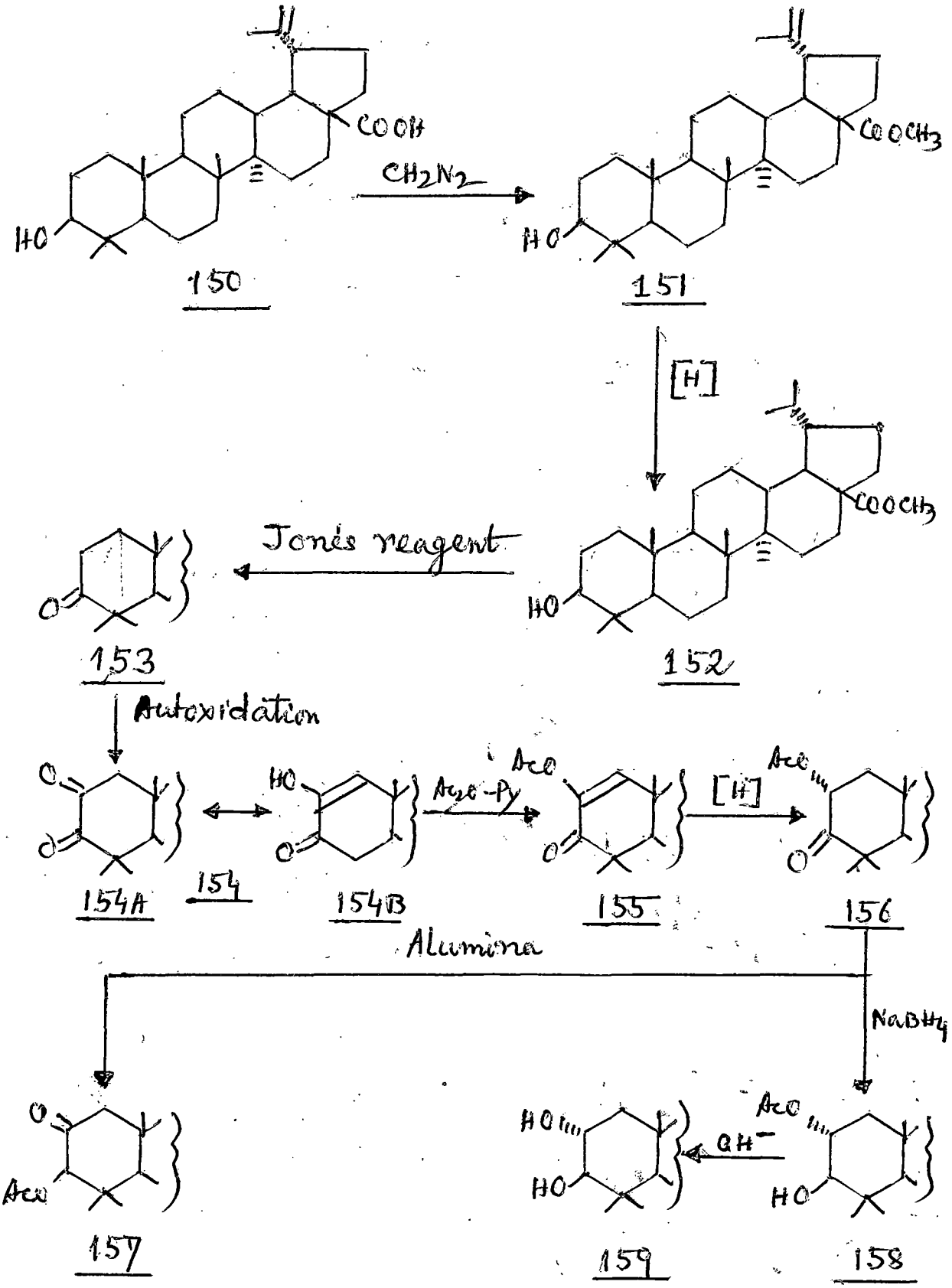
In 1968 Cheung and Feng[57] reported the partial synthesis of methyl dihydro_alphitolate by following essentially the same sequence of reactions as described by Row et al. Although the melting point of their product was same as that recorded in the literature[34] for natural dihydroalphitolate we suspect that their synthetic product was probably a mixture. They have not recorded the IR spectra of the two compounds. These anamolies prompted us to synthesise methyl dihydro_alphitolate starting from betulinic acid as described in section B.

Section B : An unambiguous synthesis of methyl dihydro-alphitolate from betulinic acid.

Betulinic acid 150 obtained by the extraction of Bischofia javanica Blume with benzene was esterified with excess diazomethane. The crude ester on chromatography and crystallisation from chloroform - methanol mixture afforded colourless needles of 151, m.p. 222 - 24°, $(\alpha)_D$ + 4°, ν_{max} 3520, 1735, 1660 and 876 cm^{-1}. 151 was found to be identical with an authentic sample of methyl betulinate by m.m.p. determination and I.R. comparison. Hydrogenation of methyl betulinate 151 in presence of Adams' catalyst gave methyl dihydrobetulinate 152, m.p. 236 - 38°, $(\alpha)_D$ - 18·6°

Jone's oxidation of methyl dihydrobetulinate furnished a

product 153, m.p. 202-4°, $(\alpha)_D$ + 8°, which was found to be identical in all respects with methyl dihydrobetulonate. Oxidation of methyl dihydrobetulonate 153, by passing oxygen through a suspension of it in tertiary butanol containing potassium tertiary butoxide (IN) afforded a product, 154, m.p. 131-3°, $(\alpha)_D$ - 1.96°. The compound showed a positive ferric chloride coloration and in the t.l.c it showed two spots of very close Rf values indicating a mixture of two tautomeric forms-the diketone 154 A and diosphenol 154 B. The UV spectram of the latter showed a maxima at 269 mμ (ϵ , 7532). The compound 154 B on acetylation with acetic anhydride - pyridine at room temperature gave the corresponding acetate 155, m.p. 194 - 96°, $(\alpha)_D$ + 9.43° which showed a single spot on chromatoplate . UV spectrum showed a maxima at 237 mμ(ϵ , 9968). These physical data and chemical properties are in good agreement with the structures 154 B and 155 for diosphenol and diosphenol acetate respectively. Hydrogenation of diosphenol acetate 155 in presence of 10 % palladium - on - charcoal catalyst gave a product, m.p. 223-25°, $(\alpha)_D$ + 32.56°. This compound has been assigned sturucture 156 on the basis of its chemical properties and in analogy to the previous work of Khastgir et al[10a,10b]. The compound 156 was kept overnight on a basic column of alumina and after eluting


COOH
CH_2N_2
HO
150
151
$COOCH_3$
[H]
Jones reagent
153
152
Autoxidation
154A
154
154B
Ac_2O-Py
AcO
155
156
Alumina
$NaBH_4$
157
159
158
OH^-

with benzene it afforded a new product, m.p. 228-30° which has been assigned structure 157, methyl-2-keto-3-acetoxy dihydrobetulinate, by analogy with previous work. This is formed by the migration of the acyl group from 2α- position to 3β- position. This type of migration has been reported in literature both in the terpenoid and steroid fields[13,17]. This fact establishes the structure of 156 as 2α- acetoxy methyl dihydrobetulonate. 2α-acetoxy methyl dihydrobetulonate 156 on sodium borohydride reduction in methanol-dioxan solution at pH 8 to reduce isomerisation gave a crystalline solid 158, m.p. 259-61°, $(\alpha)_D$ - 7.14°. The latter on a hydrolysis with a 15 % methanolic potassium hydroxide solution afforded a product which on chromatography gave a crystalline solid, 159, m.p. 230-32°. It did not show any depression in melting point when mixed with an authentic sample of methyl dihydroalphitolate supplied by Prof. E. Ritchie. The infrared spectrum of the two compounds were also found to be identical throughout the entire range.

Recently, in our laboratories, Khastgir and co-workers[10a,64] have adduced additional evidence for the α- equatorial configuration of the 2 - acetoxy group in the 2-acetoxy ketone 29 from O. R. D. studies. They have shown that the NMR spectrum of 29 showed a multiplet at δ 5.62 [39] for proton at C - 2. This downfield signal for a proton with a clear quartet of lines

(sum of J. 20 Hz) can be assumed for a methine proton α both to an acetoxy group and a carbonyl group with the acetoxy group at C - 2 position. They argued that this type of NMR signals could explain equally both for 2α-equatorial acetoxy group with the chair conformation of ring A and 2β-axial acetoxy group with the boat conformation of ring A. The 2α-equatorial configuration of the acetoxy group has been strengthened by the O. R. D. studies of the acetoxy ketones. The Octant rule[62] dictates that an α - substituent will make a significant contribution to the ketone n $\rightarrow \pi^*$ cotton effect only when in an axial orientation and the sign of the contribution will be determined by the sign of the octant in which the substituent falls. Since equatorial α -substituents lie near a symmetry plane their contribution will be insignificant. The O. R. D. of α- acetoxy ketones has been studied recently by Bull and Enslin[63] and also Klyne et al[64]. From their studies it emerged that in many cases (though not in all) the effect of an acetoxy group to the carbonyl chromophore is anti-octant i.e. the contribution of an acetoxy group to the carbonyl Cotton effect is opposite to that of an alkyl group in the same position.

In the parent ketone β -amyrone 26 the conformation of ring A is a flattened chair (to relieve the diaxial interaction

between the 10β- methyl and 4β-methyl groups) and this leads to a positive cotton effect. The same conformation is probable for the 2α-acetoxy derivative, but because of the flattening of ring A, the 2α(equatorial) acetoxy group does not lie in the nodal plane of the carbonyl group but protrudes into the back upper right octant. An alkyl group in that position would make a negative contribution to cotton effect, but the " anti-octant " acetoxy group makes a positive contribution. Thus compound 29, having a 2α-acetoxy configuration, would be expected to exhibit a more positive cotton effect. than the parent ketone β - amyrone 26. This has actually been found to be true in the present case. In the O. R. D. curve of 2α-acetoxy ketone 29 the amplitude - peak $[\phi]_{307}$ - trough $[\phi]_{269}$ has been found to be greater than that of the corresponding parent ketone (β-amyrone), peak $[\phi]_{307}$ - trough $[\phi]_{278}$. On the basis of the above evidence Khastgir and colleagues observed that the compound 29 has the 2α-equatorial acetoxy configuration. They have also stated that the alternative 2β-acetoxy configuration with the boat conformation of ring A would in all probability lead to a small negative cotton effect.

Thus our synthesis of methyl dihydroalphitolate and the configuration of the hydroxyl groups (2α, 3β) stand on

firm grounds - and we believe that this is the first unambiguous synthesis of methyl dihydroalphitolate having the same configuration and stereochemistry as the natural product.

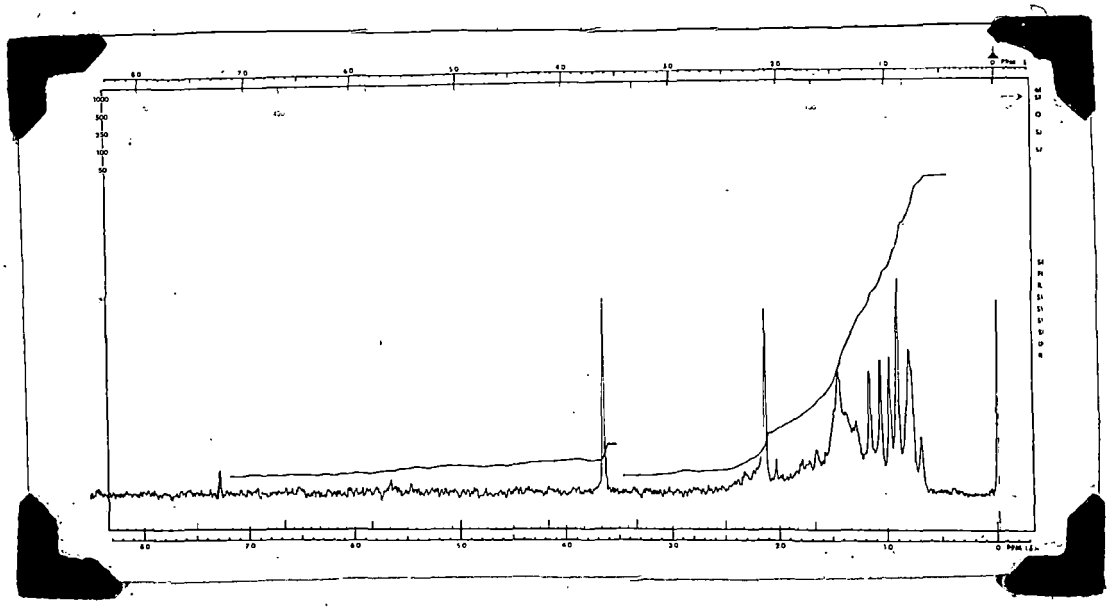


Fig. 1 : NMR spectrum of 2α-acetoxy methyl dihydrobetulonate 156

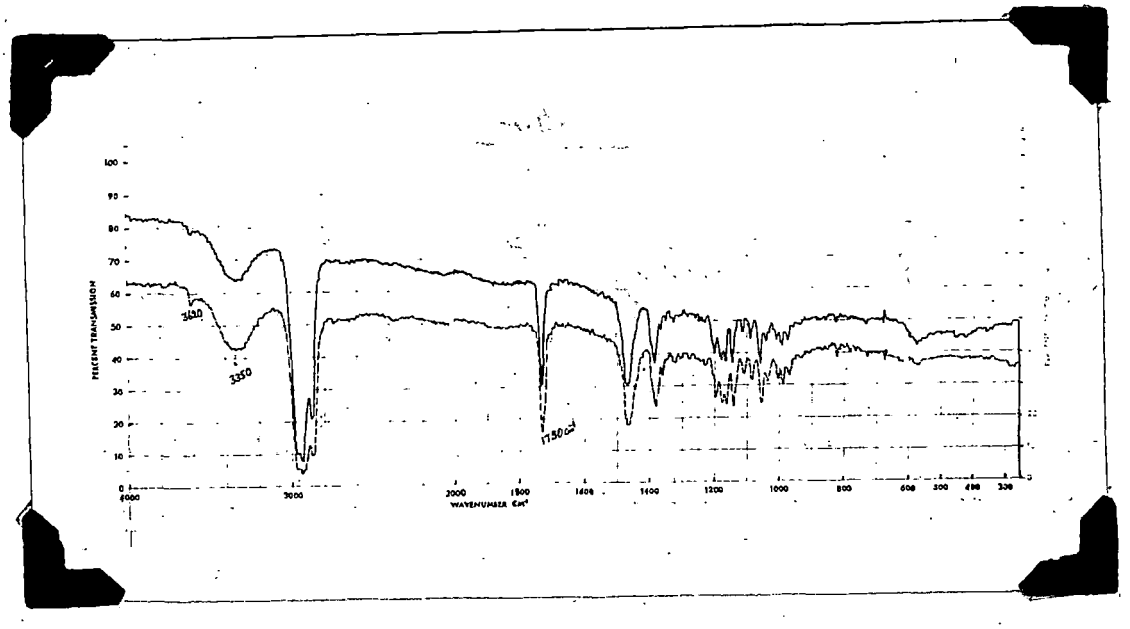


Fig. 2 : IR comparison of methyl dihydroalphitolate 159 (solid line) with an authentic specimen (dotted line)

EXPERIMENTAL

Melting points are uncorrected. The petroleum used throughout the investigation had b.p. 60 - 80°. All optical rotations were determined in chloroform solution unless stated otherwise. NMR spectra were determined on Varian A - 60 and HA - 100 spectrophotometer using chloroform - d solution containing tetramethyl-silane as reference. The IR spectra were recorded in Perkin-Elmer 337 and 221 and Beckmann IR - 20 spectrophotometers in 95% ethanol solution unless stated otherwise. TLC was done on chromatoplate of silica gel G (E. Merck) and the spots were developed with H_2SO_4 - Ac_2O (9 : 1) mixture.

Extraction of Bischofia Javanica Blume ; Isolation of betulinic Acid 150 :

Described on page 48.

Esterification of betulinic acid 150 ; Preparation of methyl betulinate 151 :

Described on page 49

Hydrogenation of methyl betulinate 151 ; Preparation of methyl dihydrobetulinate 152 ;

Described on page 50

Jones oxidation of methyl dihydrobetulinate 152 ; Preparation of methyl dihydrobetulonate 153 ;

Described on page 51

Autoxidation of methyl dihydrobetulonate 153 ; Preparation of diosphenol 154 ;

Described on page 53 .

Acetylation of diosphenol 154 ; Preparation of diosphenol acetate 155 ;

Diosphenol 154 (1 gm) was treated with acetic anhydride (10 ml) and pyridine (10 ml) and kept overnight at room temperature. After working up in the usual manner the crude acetate (0 .9 gm) was obtained. This was chromatographed over a column of alumina (60 gm) deactivated with 2.4 ml of 10%

aqueous acetic acid. The compound was dissolved in benzene (7 ml) and the chromatogram was developed with petroleum. The following solvents were used as eluent (Table - I)

Table - I

Eluent	Fractions 50 ml each	Residue on evaporation.
Petroleum [redacted]	1 - 3	Nil
Petroleum [redacted]	4 - 15	Solid (0.85 gm) m.p. 187 - 90°

Elution with move polar solvent did not afford any solid material.

Fractions 4 - 15 (0.85 gm) were combined and on crystallisation from methanol afforded needle shaped crystals of 155, m.p. 194 - 96°, $(\alpha)_D$ + 9.43°. It showed a single spot on a chromatoplate and did not respond to the colour-test with ferric chloride solution for diosphenol.

Found : C, 75,52; H, 9. 73%

Calculated for $C_{33}H_{50}O_5$: C, 75.25; H, 9.57%

UV : λ_{max} 237 mμ (ε , 9968)

Hydrogenation of diosphenol acetate 155 ;

Preparation of 2α-acetoxy-methyl dihydrobetulonate 156 ;

To diosphenol acetate 155 (1 gm) dissolved in a mixture of ethyl acetate and ethanol (30 ml each) was added 10% palladium-on-charcoal catalyst (100 mg) and the mixture was shaken in an atmosphere of hydrogen till the absorption of hydrogen ceased. The solution was filtered and after removing the solvent from the filtrate a solid residue was obtained which after crystallisation from methanol afforded 156, m.p. 223-25°, $(\alpha)_D$ + 32.56°

Found : C, 74.75 ; H, 9.97%

Calculated for $C_{33}H_{52}O_5$: C, 74.96 ; H, 9.91%

NMR (60Mc) / Fig - 1

Sodium borohydride reduction of 2α-acetoxy-methyl dihydrobetulonate 156 ; Preparation of 2α-acetoxy-methyl dihydrobetulinate 158 :

The 2α-acetoxy-methyl dihydrobetulonate 156 (200 mg)

dissolved in a mixture of dioxan and methanol (10 ml each), was added, with cooling a slurry of sodium borohydride (200 mg) prepared in an NH_4Cl - NH_4OH buffer (pH = 8, 3 ml) and the mixture was stirred at room temperature for three hours. Most of the solvents were removed by distillation, cooled and acidified with dilute hydrochloric acid and then extracted with ether. The ethereal layer was washed with water till neutral and dried (Na_2SO_4). Removal of ether gave a solid residue (150 mg) which was chromatographed over a column of alumina (25 gm, deactivated with 1 ml of 10% aqueous acetic acid). The residue was dissolved in benzene, poured on the column and was eluted with the following solvents (Table - II).

Table - II

Fluent	Fractions 50 ml each	Residue on evaporation
Petroleum	1 - 4	Oil (15 mg)
Petroleum : benzene (4 : 1)	5 - 7	Nil
Petroleum : benzene (3 : 2)	8 - 12	Solid (100 mg) m.p. 254 - 57°

Further elution with more polar solvent did not afforded any solid material.

Fractions 8 - 12 (100 mg) were combined and on crystallisation from methanol furnished pure 2α-acetoxy-methyl dihydrobetulinate 158, m.p. 259 - 61°, $(\alpha)_D$ - 7.14°.

Found: C, 74.43; H, 10.02%

Calculated for $C_{33}H_{54}O_5$: C, 74.67; H, 10.25%

IR :

Hydrolysis of 2α- acetoxy-methyl dihydrobetulinate 158

Preparation of methyl dihydroalphitolate 159 :

To 2α- acetoxy-methyl dihydroalphitolate 158 (200 mg) was added 15% methanolic potassium hydroxide (20 ml) and the mixture was heated under reflux for three hours. The reaction mixture, after removal of solvent, was diluted with water and then extracted with ether. The ethereal layer was washed with water till neutral and dried (Na_2SO_4). The solvent was removed and a solid residue (180 mg) was obtained. This residue dissolved in benzene was placed over a column of alumina (15 gm. deactivated with 0.6 ml of 10% aqueous acetic acid) developed with petroleum and was eluted with the following solvents (Table - III)

Table - III

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum	1 - 3	Oil (trace)
Petroleum : Benzene (4 : 1)	4 - 7	Nil
Petroleum : benzene (3 : 2)	8 - 11	Solid (10 mg) m.p. 259-61° (unreacted)
Petroleum benzene (1 : 4)	12-14	Nil
Benzene	15-17	Nil
Benzene : Ether (4:1)	18-21	Solid (150 mg) m.p. 228-30°.

Further elution with more polar solvent did not yield any solid meterial.

Fractions 18-21 (150 mg) were combined and on crystallisation from methanol furnished pure methyl dihydroalphitolate 159, 230-32°. This compound showed no depression of melting point on

admixture with an authentic sample supplied by Prof. E. Ritchie. The infrared spectrum of the compound also found to be identical throughout the entire range.

Found :	C, 76.32; H, 10.55%
Calculated for $C_{31}H_{52}O_4$:	C, 76.18; H, 10.72%

IR : 3620, 3350, 1730 cm^{-1}

Isomerisation of 2α-acetoxy methyl dihydrobetulonate 156 ; Preparation of 2 keto - acetyl-methyl dihydrobetulinate 157 ;

2α- acetoxy methyl dihydrobetulonate 156 (100 mg) dissolved in benzene (3 ml) was adsorbed on a column packed with basic alumina (Brockman) and left overnight. Next day it was eluted with benzene and the solid obtained was crystallised from methanol, m.p. 226-28°. This compound on admixture with the starting material melted at 196 - 98°.

Fund :	C, 74.69; H, 10.02%
Calculated for $C_{33}H_{52}O_5$:	C, 74.96; H, 9.91%

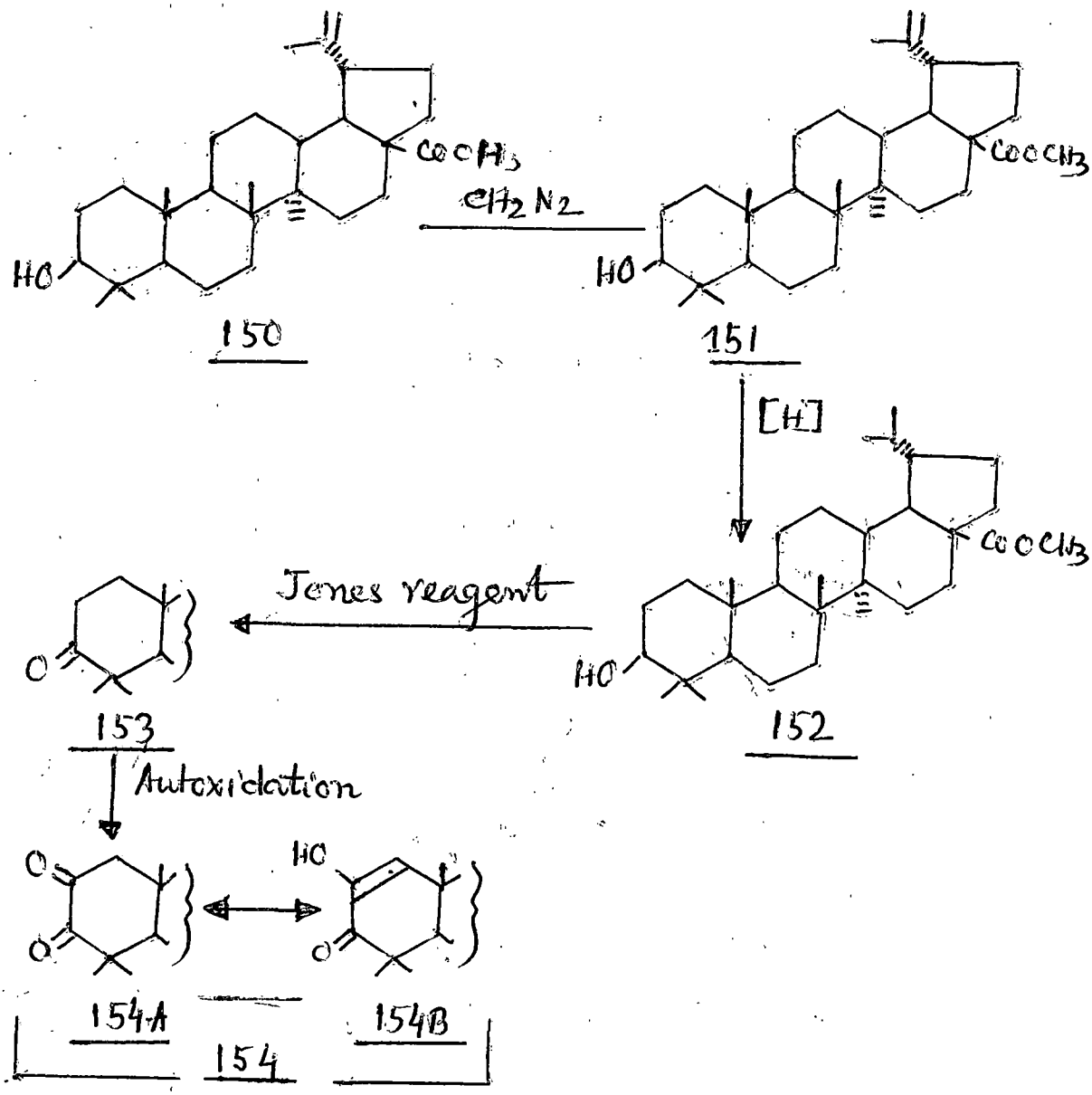
Section C : Synthesis of methyl 2β, 3β- dihydroxy betulinate from betulinic acid.

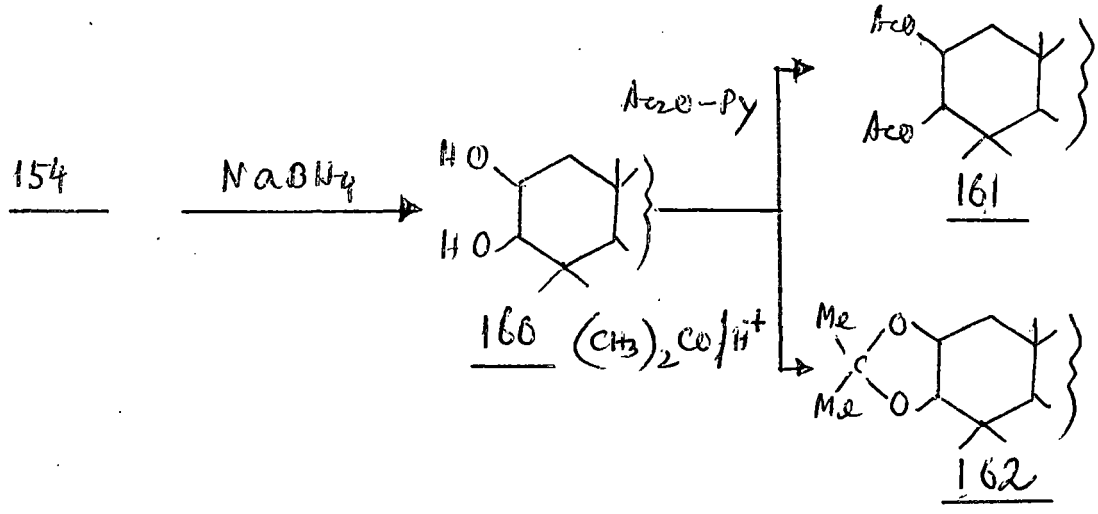
The preparation of the diosphenol 154 starting from betulinic acid 150 has already been discussed (page 48-54). Diosphenol 154 on sodium borohydride reduction in methanol solution gave a compound 160, m.p. 261-63°, $(\alpha)_D$ 21.62°, no UV absorption in the region 220-300ø mμ. ν_{max} 3525, 3360, 1720 cm^{-1}. Treatment of 160 with pyridine and acetic anhydride gave the diacetate 161, m.p. 186-87°, ν^{KBr}_{max} 1745, 1720, 1258 cm^{-1}. Examination of the NMR spectrum of 160 showed a multiplet at 3.20 ppm assigned to $C_{(3)}$- 3H and a broad unresolved multiplet at about 4.5 ppm ($C_{(2)}$- 2H) which collapsed to a doublet (J = 3.7 Hz) and a multiplet ($\leq$J - 6H_z) respectively upon exchange of hydroxyl proton with D_2O. Thus the hydroxyl group at C - 3 is equatorial (Ha) and the one at C - 2 is axial (He). In the NMR spectrum of its diacetate 161, these signals were shifted to a downfield to 4.8 ppm (doublet, J = 4Hz) and at about 5.4 ppm (broad multiplet). The signals for the ester group and the acetate group appeared at 3.65 ppm (singlet, 3H) and at 2.06 (singlet 6H) ppm.

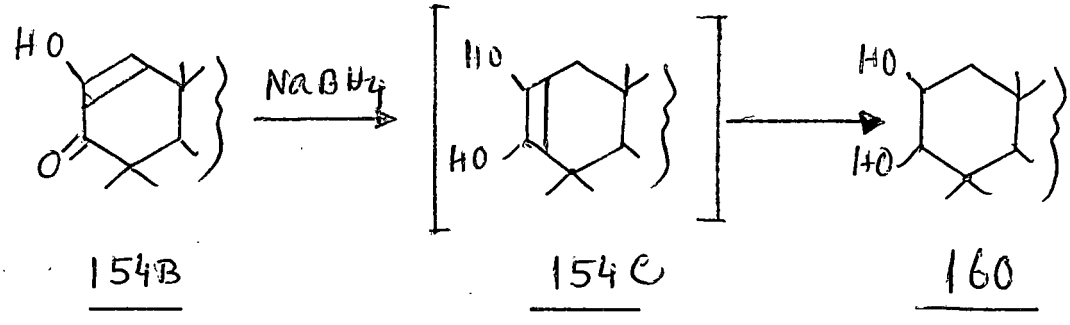
Sodium borohydride reduction would be expected to furnish a 2α, 3α-diol, or 2β, 3β-diol or a mixture of

2α, 3β and 2α, 3α diols. However, 2β, 3β- diol 160 could only be isolated which can be explained if it is assumed that the reduction proceeds via the intermediate 154 C

The diol 160 on treatment with acetone in presence of catalytic amount of p-toluene sulfonic acid gave an acetonide derivative 162, m.p. 194-95°.




154
NaBH4
HO
HO
160
Ac2O-Py
AcO
AcO
161
(CH3)2CO/H+
Me
Me
O
O
C
162


HO
O
154B
NaBH4
HO
HO
154C
HO
HO
160

EXPERIMENTAL

Melting points are uncorrected. The petroleum ether used throughout the investigation had b.p. 60-80°. All optical rotations were determined in chloroform solution unless stated otherwise. NMR spectra were determined on Varian A - 60 and HA - 100 spectrophotometers using chloroform - d solution containing tetramethyl silane as reference. The IR spectra were recorded in Perkin - Elmer 337 and 221 and Beckmann I.R - 20 spectrophotometers. UV absorption spectra were taken in Ziess VSU - 1 and UV Beckmann DU - 2 spectrophotometers using 95% ethanol solution unless otherwise stated.

Sodium borohydride reduction of diosphenol 154 : Preparation of methyl 2β,3β - dihydroxy betulinate 160 :

To a solution of diosphenol 154 (200 mg) in methanol (100 ml) sodium borohydride (200 mg) was added and the mixture was stirred for 4 - hours. The reaction

mixture was concentrated, diluted with water and then acidified with dilute hydrochloric acid (6 ml) when a solid precipitated out . The solid (100 mg) was dissolved in benzene and was poured on a column of alumina (10 gm , deactivated with 0.4 ml of 10% aqueous acetic acid) developed with petroleum. The chromatogram was eluted with the following solvents (Table - IV)

Table - IV

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum	1 - 2	Nil
Petroleum : benzene (3 : 1)	3 - 4	Nil
Petroleum : benzene (1 : 1)	5 - 6	Nil
Petroleum : benzene (1 : 3)	7 - 8	Nil
Benzene	9 - 14	Solid (180 mg) m.p. 256-58^{o}

Elution with more polar solvent did not yield any solid material.

Fractions 9 - 14 (180 mg) were collected and crystallisation from a mixture of chloroform and methanol afforded needle shaped crystals of 160, m.p. 261-63°, $(\alpha)_D$ + 21.62°.

Found : C, 76.49; H, 10.47%

Calculated for $C_{31}H_{52}O_4$: C, 76.18; H, 10.72%

UV : No absorption in the region 220-300 mμ

IR : ν_{max} 3525, 3360, 1720 cm^{-1}

NMR (60 Mc/S): Peaks at 3.15 (multiplet) and 4.4 (multiplet), 5.15 ppm.

Acetylation of methyl 2β, 3β- dihydroxy betulinate 160 ; Preparation of methyl 2β, 3β- diacetoxy betulinate 161 :

The diol 160 (200 mg) was acetylated by heating with pyridine (4 ml) and acetic anhydride (4 ml) on a water bath for four hours. After working up in the usual manner it gave a solid residue (180 mg). This residue dissolved in benzene was placed over a column of alumina (15 gm, deactivated with 0 . 6 ml of 10% aqueous acetic acid) developed with petroleum and was eluted with the following solvents (Table - V).

Table - V

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum	1 - 5	Solid (170 mg) m.p. 181-4°

Further elution with more polar solvent did not yield any solid material.

Fractions 1 - 5 (170 mg) were combined and on crystallisation from a mixture of chloroform and methanol furnished colourless needles of **161**, m.p. 186 - 87°

Found : C, 73.54; H, 9.71%

Calculated for $C_{35}H_{56}O_6$: C, 73.39; H, 9.85%

UV : No absorption in the region 220 - 300 mμ

IR : ν_{max} 1258, 1720, 1745 cm^{-1}

NMR (60 Mc/s) : Peaks at 3.65 (singlet, COOMe)
2.06 (singlet, 6 H), 4.6, 5.4 ppm.

Preparation of acetonide 162 of methyl 2β, 3β- dihydroxy betulinate 160 :

To 2β, 3β- diol 160 (100 mg) dissolved in dry acetone (20 ml) was added a few crystals of p - toluene sulfonic acid and the mixture was shaken for 10 - minutes and then kept overnight. After usual work up it gave a solid residue (80 mg). This product dissolved in benzene (3 ml) was placed over a alumina column (10gm, deactivated with 0.4 ml of 10% aqueous acetic acid) developed with petroleum and was eluted with the following solvents (Table - VI).

Table - VI

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum	1 - 3	Solid (70 mg) m.p. 192 - 4°

Elution with more polar solvent did not yield any solid material.

Fractions 1 - 3 (70 mg) were combined and crystallisation from methanol afforded pure crystals of acetonide derivative 162 m.p. 194 - 95°.

Found :	C, 77.45 ; H, 10.73%
Calculated for $C_{34}H_{56}O_4$:	C, 77.22 ; H, 10.67%

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