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TERPENOIDS—LXXXVI

STRUCTURE OF EPI-ψ-TARAXASTANONOL AND EPI-ψ-TARAXASTANEDIOL*

V. K. HINGE, S. K. PAKNIKAR, K. G. DAS†, A. K. BOSE† and S. C. BHATTACHARYYA
National Chemical Laboratory, Poona, India

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Abstract—Two new pentacyclic triterpenes of the taraxastane group have been isolated from *Canarium strictum* Roxb. One is a ketol and the other a diol. Chemical evidence, IR, UV, NMR spectra and their mass spectral disintegration patterns show that they are represented by the structures I and IIa. They have been named as epi-ψ-taraxastanonol and epi-ψ-taraxastane diol respectively.

IN a preliminary communication[1] on the Indian black dammar resin (*Canarium strictum* Roxb.), the isolation of two new polyterpenes, a ketol and a diol was reported.

In this paper, chemical evidence, supported by IR, UV, NMR and mass spectral data, confirm that the ketol is represented by structure I and the diol by structure IIa. Both triterpenes belong to the taraxastane group. Because of their epimeric relationship to ψ-taraxastanediol, obtained earlier from *Manila elemi* resin,[2] the ketol is named epi-ψ-taraxastanonol and the diol epi-ψ-taraxastane diol.

Epi-ψ-taraxastane diol, has been proved homogeneous by rigorous column chromatography, crystallization and TLC. Elemental analysis suggests the molecular formula, $C_{30}H_{52}O_2$, which is supported by the mass spectral determination of the mol. wt. of the monoacetate. Spectral evidence, as well as a negative tetranitromethane test, indicate that it is a saturated compound. It shows IR (Fig. 1) absorption band at 3472 cm^{-1} for the hydroxyl group. On acetylation, it forms a crystalline monoacetate with the molecular formula $C_{32}H_{54}O_3$. This shows IR (Fig. 1) absorption at 3623 (—OH) and 1730 cm^{-1} (OAc). One of the hydroxyl groups in the diol therefore is resistant towards acetylation and is presumably tertiary. The IR absorption band at 3623 cm^{-1} for the hydroxyl group[3] of the monoacetate would also suggest the presence of a tertiary hydroxyl group.

In its general properties the diol is closely related to taraxastane derivatives. This is in analogy with the occurrence of ψ-taraxasterol in the resin. In conformity with this, epi-ψ-taraxastane diol monoacetate with thionyl chloride undergoes facile dehydration[4] to afford ψ-taraxasterol acetate (IIIb), with characteristic IR absorption

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† Prof. A. K. Bose and Dr. K. G. Das, both of the Stevens Institute of Technology, Hoboken, New Jersey, U.S.A. have carried out the determination of mass spectra and their interpretation.

[1] V. K. Hinge, A. D. Wagh, S. K. Paknikar and S. C. Bhattacharyya *Tetrahedron* **21**, 3197 (1965).

[2] M. Morice and C. E. Simpson, *J. Chem. Soc.* 795 (1940); and 181 (1941); J. L. Simonsen and W. C. J. Ross, *The Terpenes* Vol. IV; p. 167, Cambridge Univ. Press (1957).

[3] K. W. Benteley, *Technique of Organic Chemistry* Vol. XI; p. 146. Interscience, New York (1963); C. S. Chopra (the late), D. E. White and (in part) G. J. H. Metrose, *Tetrahedron* **21**, 2585 (1965).

[4] E. von Rudloff, *Canad. J. Chem.* **39**, 1860 (1961).

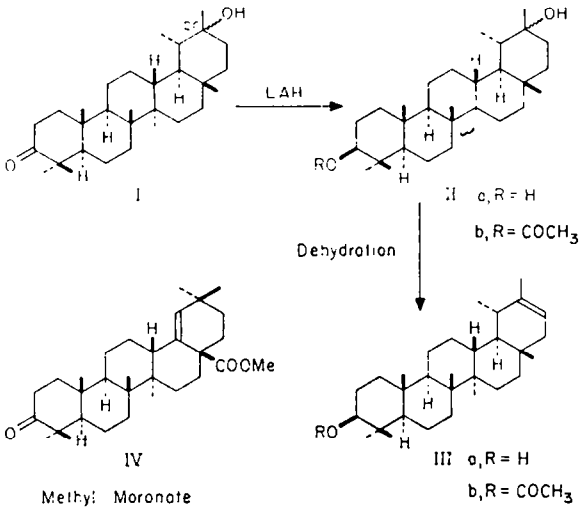


CHART – I

band at 785 cm^{-1} for the trisubstituted double bond.[5] This clearly shows that epi-ψ-taraxastane diol has a carbon skeleton identical to ψ-taraxasterol with the secondary hydroxyl group at C_3 and the tertiary hydroxyl group, necessarily, located at C_{20}. Epi-ψ-taraxastane diol is therefore represented by the structure IIa. This structure is fully supported by the NMR spectrum* as well as the mass spectral data.

The NMR spectrum[6] (Fig. 2) shows signals at 49·0, 51·0, 52·5, 58·5 c/s (15H) due to the methyl groups at C_8, C_{10}, C_{14}, C_{17} and C_{19}. The signal at 63·5 c/s (6H) is due to the *gem*-dimethyl grouping at C_4. The signal at 68 c/s (3H) is due to the methyl group at C_{20}, which is on a carbon atom carrying a tertiary hydroxyl group. It also shows a signal at 119 c/s (3H), which is due to the acetate methyl group.

Morice and Simpson[2] have isolated from *Manila elemi* resin a crystalline diol, the monoacetate of which on dehydration gives ψ-taraxasterol acetate (IIIb). This compound has also been assigned the structure IIa. Careful comparison of the properties of the diol and its monoacetate obtained from the Indian black dammar resin with those of the diol and the monoacetate from the *Manila elemi* resin, reveals that these two products are identical, the only difference being that the tertiary hydroxyl groups at C_{20} are epimeric. The properties of the compounds of these two series are compared below.

Source	Diol		Monoacetate	
	m.p.	$(\alpha)_D$	m.p.	$(\alpha)_D$
1. *Manila elemi* resin	270-272°	−10·9°	281-284°	− 1·5°
2. Indian black dammar resin	261-263°	±0°	266-267°	+23·4°

* We are grateful to Prof. R. B. Bates, University of Arizona, U.S.A., for the determination of the NMR spectrum.

[5] J. L. Simonsen and W. C. J. Ross, *The Terpenes* Vol. IV; p. 167, Cambridge Univ.; S. K. Paknikar, Ph.D. Thesis, University of Poona (1962).

[6] M. Shamma, E. Glick and O. Mumma, *J. Org. Chem.* **27**, 4512 (1962).

Epi-ψ-Taraxastanonol (I) is also a crystalline compound, with the molecular formula $C_{30}H_{50}O_2$, which is confirmed by the mass spectral determination. Its IR spectrum (Fig. 1) shows bands at 3484 cm^{-1} (OH) and 1689 cm^{-1} (>C=O). It resists acetylation under normal conditions, indicating the presence of a tertiary hydroxyl group. IR, UV and NMR spectral measurements and negative colour reaction with tetranitromethane would suggest the saturated nature of the product. It forms a crystalline oxime.

From its general behaviour it was also suspected to be a taraxastane derivative. On reduction with LAH it affords epi-ψ-taraxastane diol (IIa). It is therefore represented by the structure I.

The structure is supported by its NMR spectrum[6] (Fig. 2), which shows signals at 51·5 and 57 c/s (3H) due to the secondary methyl group at C_{19}. Signals at 58, 62, 66 c/s (18H) are observed due to the methyl groups at C_4, C_8, C_{10} and C_{17}. Signal at 72 c/s (3H) is exhibited due to the methyl group at C_{20}, which is on a carbon atom carrying a tertiary hydroxyl group. In addition to these, signals at 142, 143, 147, 148, 149 and 150 c/s (2H) are observed due to the presence of two protons adjacent to the carbonyl group at C_3.

In further support of the structures I and IIa the mass spectral fragmentation pattern of the ketol and the diol monoacetate have been studied (Fig. 3; Charts 2 and 3).

Mass spectral study of epi-ψ-taraxastanonol (I) *and epi-ψ-taraxastane diol monoacetate* (IIb)

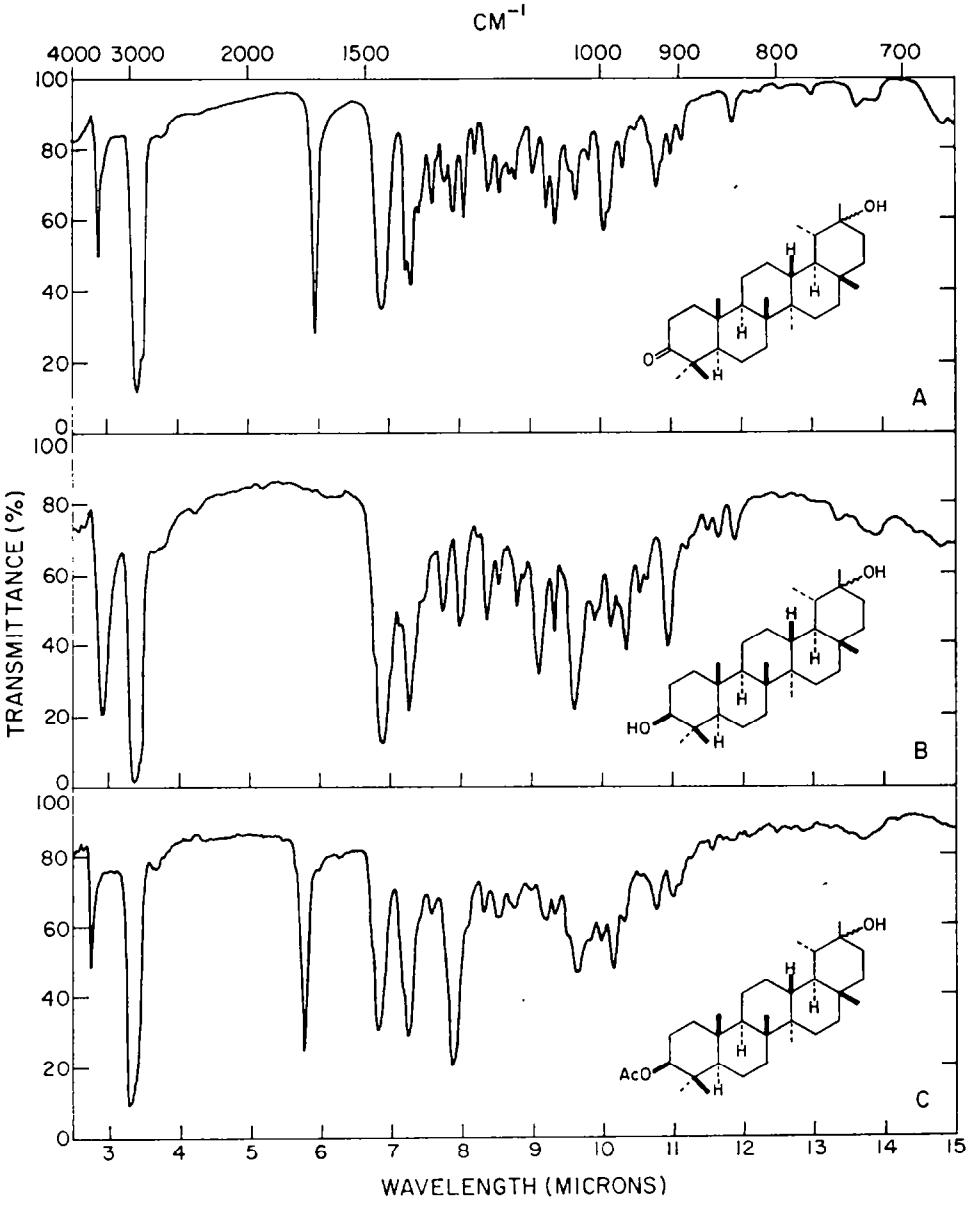
Mass spectrometry has been recently employed for the elucidation of the structure of polycyclic natural compounds,[7–9] including ψ-taraxasterol and related products.[10]

In the mass spectrum (Fig. 3) of I, the molecular ion is not observed. The heaviest fragment (A) (*m/e* 424) observed corresponds to the loss of a mole of water (M-18 = 424). The peaks (B) at *m/e* 342 and (C) at *m/e* 82, due to retro Diels-Alder type of fragmentation, are observed during the cleavage of the ring E.

According to Djerassi *et al.*,[10] cleavage of the ring 'C' in methyl moronate (IV) yields a fragment (D) *m/e* 205. In the mass spectrum of I, a significant peak (D) at *m/e* 205 was observed. This indicates the structural similarity between the compounds I and IV in the rings A, B and C. Moreover, peaks at *m/e* 177 (D-28) and *m/e* 135 (D-70), which could be formed from the fragment (D) with *m/e* 205 as a result of the loss of the carbonyl and that of carbonyl and *gem*-dimethyl groups $\left(O{=}C{-}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$, are observed in the spectrum. This clearly indicates the presence of a carbonyl function at C_3. This is in agreement with the chemical evidence obtained.

In the mass spectrum (Fig. 3) of IIb, the molecular ion is not observed. The heaviest fragment (A) observed is at *m/e* 468, which corresponds to the loss of a mole of water from the molecular ion (M-18 = 468). The tertiary hydroxyl group present in the compound presumably undergoes dehydration to produce the fragment

[7] P. deMayo and R. I. Reed, *Chem. & Ind.* 1481 (1956).
[8] R. I. Reed, *J. Chem. Soc.* 3432 (1958).
[9] C. Djerassi, H. Budzikiewicz and J. M. Wilson, *Tetrahedron Letters* 263 (1962).
[10] H. Budzikiewicz, J. M. Wilson and C. Djerassi, *J. Amer. Chem. Soc.* **85**, 3688 (1963).



FIG·I· IR SPECTRA OF:-(A)-EPI-ψ-TARAXASTANONOL ;(B)-THE DIOL AND (C)-THE DIOL MONOACETATE·

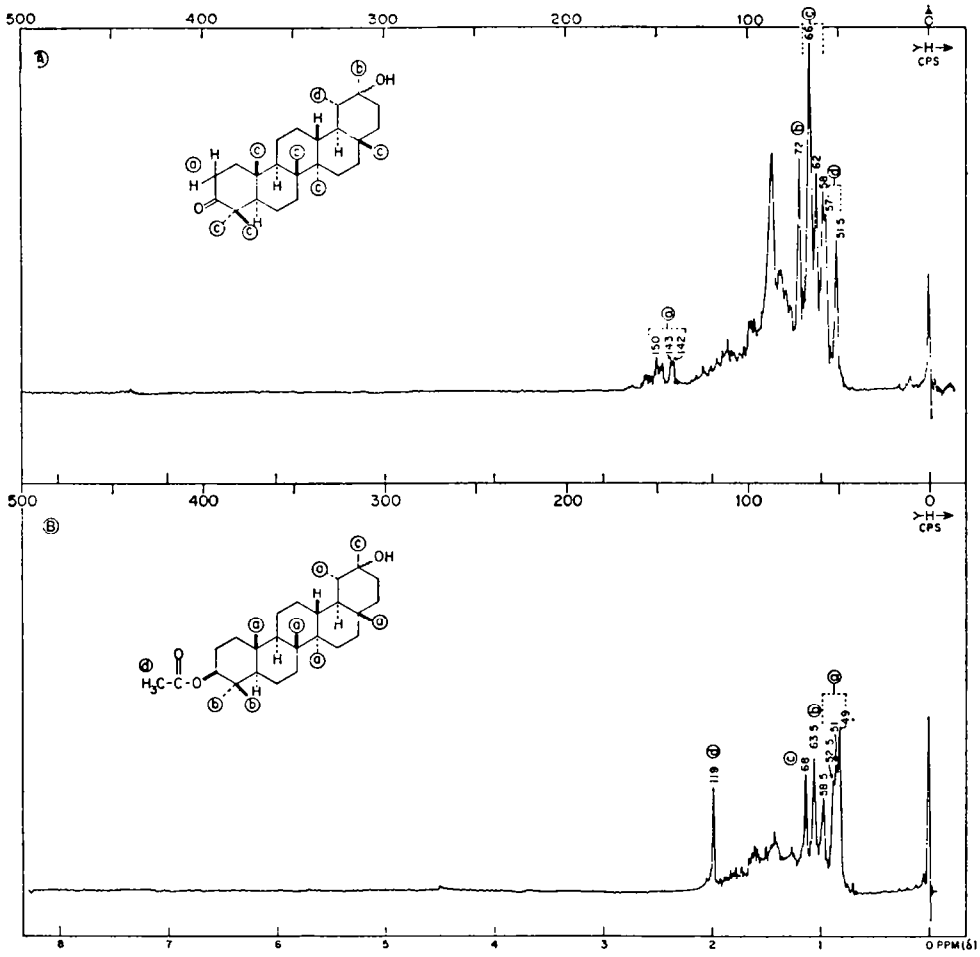


FIG. 11 NMR SPECTRA OF (A) EPI-ψ-TARAXASTANONOL and (B) EPI-ψ-TARAXASTANE DIOL MONOACETATE

(A) *m/e* 468. A comparison of the mass spectrum of IIb and IIIb shows that the two spectra are superimposable.

The similarity in the spectra of compounds IIb and IIIb suggests that IIb undergoes dehydration to give IIIb, with the formation of a double bond at $\Delta^{20,21}$. If the dehydration follows a different route, the resulting product will give a different fragmentation pattern. This indicates that IIb has a tertiary hydroxyl group at C_{20} and that under electron impact IIIb is a probable intermediate.

From the comparison of the mass spectra (Fig. 3) of I and IIb, the possible mode of fragmentation under electron impact of epi-ψ-taraxastanonol (I) can be represented as shown in Charts 2 and 3.

EXPERIMENTAL

All m.ps are uncorrected. Rotations were measured in $CHCl_3$. The pet. ether refers to the fraction boiling between 60–80°. Neutral alumina graded according to the Brockmann-procedure[11,12]

[11] H. Brockmann and H. Lederer, *Ber. Dtsch. Chem. Ges.* **74**, 73 (1941).
[12] E. Lederer and M. Lederer, *Chromatography* p. 26. Elsevier, Amsterdam (1957).

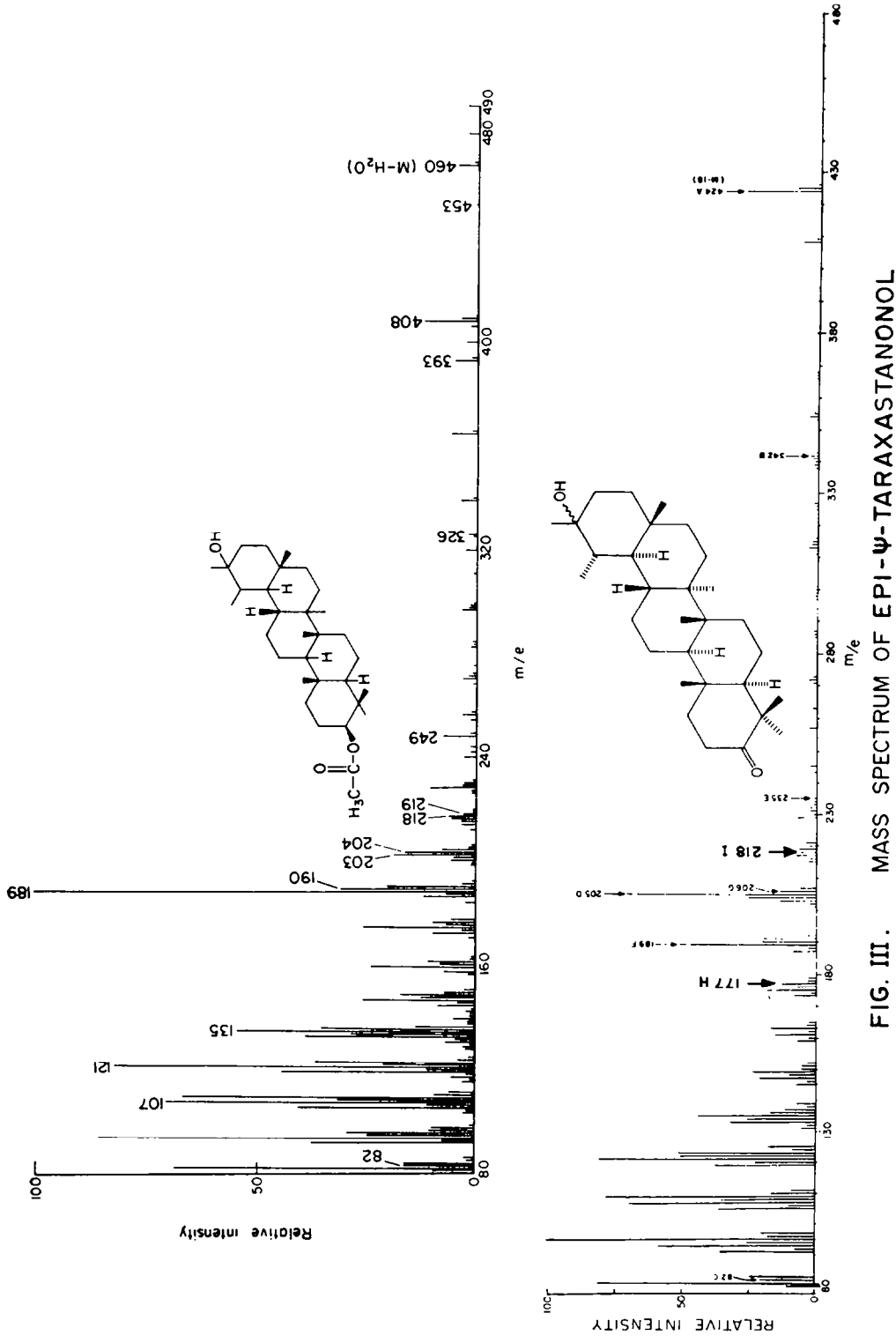


FIG. III. MASS SPECTRUM OF EPI-Ψ-TARAXASTANONOL

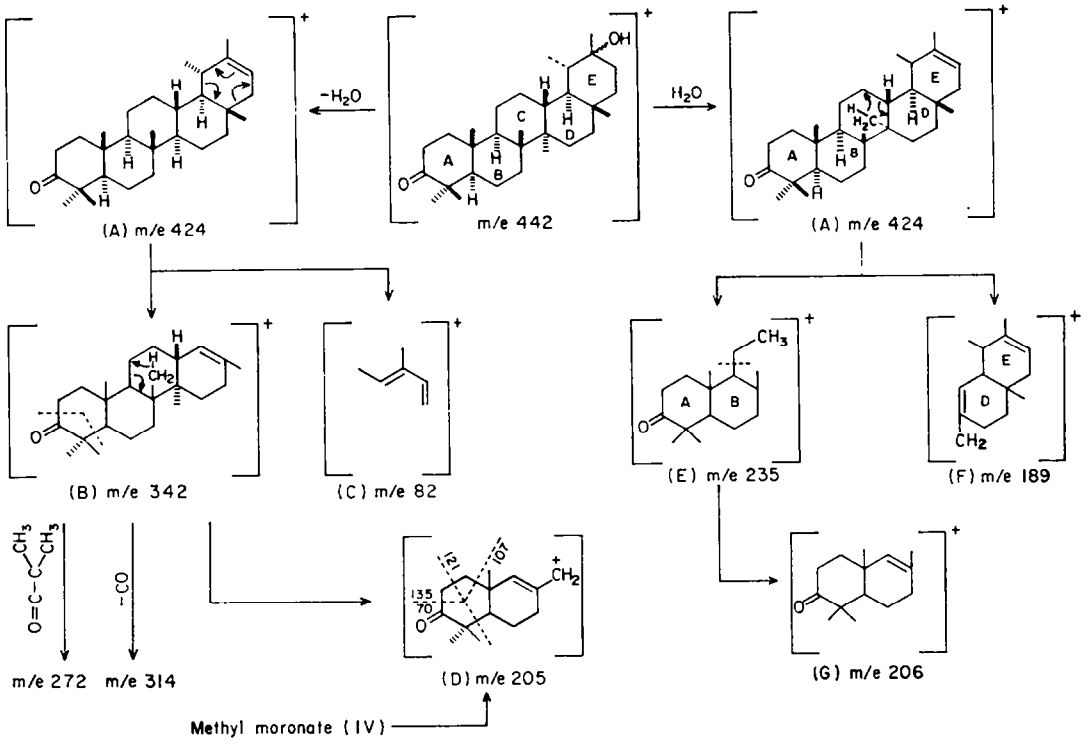


Chart-2

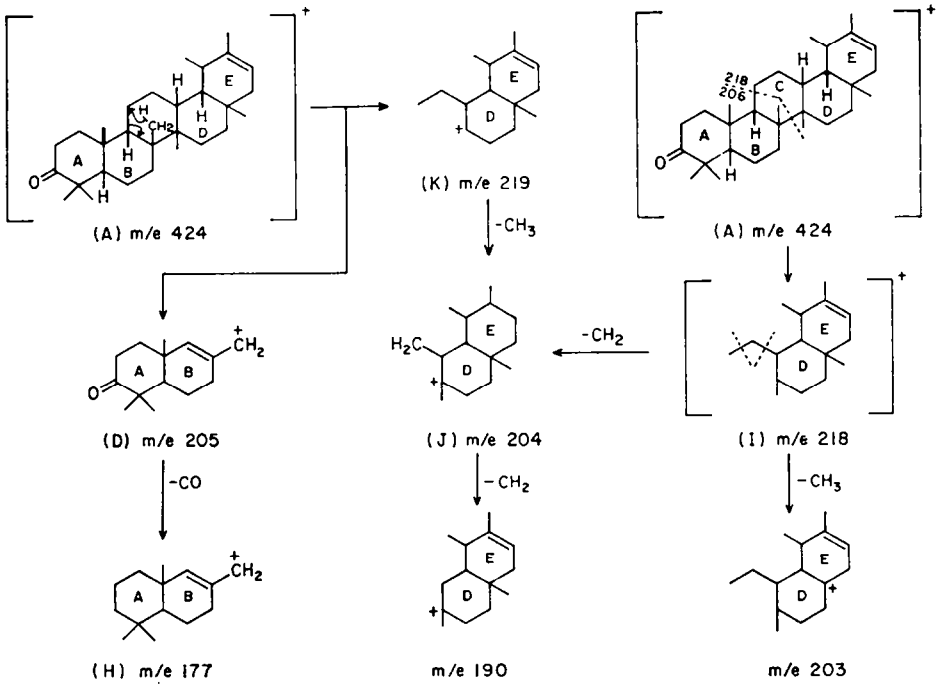


Chart-3

was used in chromatography. UV spectra were recorded in alcohol solution on Beckman DK-2 ratio recording spectrophotometer by H. Gopinath. IR spectra in nujol mull, were determined with Perkin-Elmer model No. 137-B, IR spectrophotometer, using NaCl optics by K. G. Deshpande. The NMR spectra were taken by Mr. Mulla in CCl_4, unless otherwise stated, using TMS as internal reference on a 60 Mc Varian instrument and the chemical shifts were measured in c/s units. Microanalyses were carried out by Mr. Pansare and colleagues. Mass spectra were run on CEC-21-103 C mass spectrometer by K. G. Das using all glass heated inlet system. The spectra were run at 70 ev.

Isolation of epi-ψ-taraxastanonol (I) *and epi-ψ-taraxastane diol* (IIa). These two products were isolated from the tail fractions of the main chromatography described in the previous communication. The earlier tail fractions contained I and the later tail fractions contained IIa. The respective fractions on standing for about a month deposited crystals which were recrystallized from benzene to give the pure ketol and the diol.

epi-ψ-Taraxastanonol (I). The homogeneity of this crystalline compound, m.p. 257–59°, $[\alpha]_D$ + 25·3° (*c*, 2·96) was confirmed by column chromatography, crystallization and TLC analysis. Elemental analysis suggested the molecular formula, $C_{30}H_{50}O_2$. IR, UV, NMR spectral data, as well as tetranitromethane test, indicated the saturated nature of the compound. IR spectrum (Fig. 1) exhibited bands at 3484, 2941, 2857, 1689, 1453, 1389, 1372, 1316, 1266, 1249, 1220, 1190, 1170, 1107, 1087, 1071, 1036, 997, 972, 926, 910, 898 and 844 cm^{-1}. (Found: C, 81·53; H, 11·69. $C_{30}H_{50}O_2$ requires: C, 81·39; H, 11·38%.)

Preparation of oxime. A solution of hydroxylamine hydrochloride (0·125 g), 10% NaOHaq (0·5 ml), and I (50 mg) in dil. EtOH was refluxed for 20 min and cooled in ice to yield the oxime which when crystallized from EtOH–benzene afforded the pure oxime, m.p. 267–269° (dec). IR spectrum showed bands at: 3509, 3322, 2967, 2899, 1460, 1374, 1344, 1168, 1087, 1016, 998, 965, 923, 918, 895 and 846 cm^{-1}. (Found: N, 3·42. $C_{30}H_{51}O_2N$ requires: N, 3·06%.)

Lithium aluminium hydride reduction of the ketol (I) *in tetrahydrofuran.* To a cooled solution of LAH (0·1 g) in freshly distilled THF (15 ml) a solution of I (54 mg) in THF (15 ml) was added drop by drop. The reaction mixture was then stirred under cooling for 1 hr and then refluxed for 5 hr. Unreacted LAH was decomposed first by addition of moist ether and then by water. Removal of the solvent afforded IIa, which on acetylation (pyridine–Ac_2O at the room temp overnight) afforded IIb, which was crystallized from pet. ether, m.p. 265–266°; $[\alpha]_D$ + 23·4° (*c*, 0·47). IR spectrum (Fig. 1) showed bands at: 3623, 3030, 1730, 1468, 1383, 1319, 1271, 1202, 1165, 1142, 1112, 1088, 1074, 1039, 1002, 985, 972, 926, 910, 904, 867 cm^{-1}. (Found: C, 78·71; H, 11·12. $C_{32}H_{54}O_2$ requires: C, 78·96; H, 11·18%.)

Epi-ψ-taraxastane diol (IIa). This was isolated in the crystalline form from the tail fractions of the main chromatography. When crystallized from benzene pure diol was obtained, m.p. 261–263° $[\alpha]_D \pm 0°$. The purity was confirmed by TLC (silica gel; 15% AcOEt in pet. ether). Elemental analysis suggested the molecular formula, $C_{30}H_{52}O_2$, which was also confirmed from the mol wt indicated from mass spectral data. IR spectrum (Fig. 1) exhibited bands at: 3472, 2994, 2924, 1460, 1385, 1295, 1258, 1198, 1175, 1139, 1101, 1073, 1044, 990, 968, 951, 916, 892, 860 and 842 cm^{-1}. (Found: C, 80·56; H, 11·75. $C_{30}H_{52}O_2$ requires: C, 81·02; H, 11·79%.) No colour was observed with tetranitromethane in $CHCl_3$ and no absorption was observed in the UV spectrum, indicating the saturated nature of the diol.

Acetylation of the diol (IIa). Compound IIa (0·1 g) was dissolved in pyridine (2 ml), Ac_2O (2 ml) was added and the mixture kept overnight at the room temp. It was then added with stirring into ice cold water and extracted with ether. The extract was washed thoroughly with water and dried over Na_2SO_4. On removal of the solvent, epi-ψ-taraxastane diol monoacetate was obtained and purified by crystallizing from pet ether, m.p. 266–267°, $[\alpha]_D$ + 23·0° (*c*, 0·8). Elemental analysis corresponded to the molecular formula, $C_{32}H_{54}O_2$, which was confirmed by mass spectral evidence. The IR spectrum was found to be superimposable on that of the diol monoacetate obtained by LAH reduction of I, and acetylation.

Dehydration of epi-ψ-taraxastane diol monoacetate (IIb) *by thionyl chloride.* A solution of IIb (20 mg) in pyridine (3 ml) was cooled to 5° and $SOCl_2$ (0·3 ml) added dropwise with shaking. The mixture was kept for 15 min with occasional shaking. Removal of the solvent afforded a solid material which on crystallization from AcOEt gave ψ-taraxasterol acetate, m.p. and mixed m.p. 226–228°. The IR spectrum was superimposable with that of ψ-taraxasterol acetate.