CHAPTER 2

ISOLATION AND STRUCTURE ELUCIDATION OF ODOLACTONE, A NEW TRITERPENOID

SECTION A

PRELIMINARY INVESTIGATION ON ODOLACTONE

Isolation of odolactone — a new triterpenoid lactone

Air dried powdered bark of Gynocardia Odorata (R Br) was exhaustively extracted with benzene in Soxhlet apparatus for 36 hours. The extract was evaporated under reduced pressure to give a gummy residue. The residue was extracted with ether, the ether insoluble portion on repeated crystallizations from chloroform-methanol mixture furnished a colourless semi-amorphous solid, having mp $> 320^{\circ}$,* $[\alpha]_D$ $- 47.06^{\circ}$, which has been shown to be a new pentacyclic triterpenoid, named odolactone.

The ether solution was washed with 10% aqueous sodium hydroxide and then with water till it was neutral. The neutral ethereal solution was dried over anhydrous sodium sulphate and it was evaporated to dryness to yield a gummy residue which constituted the neutral part of the extract.

The alkali washed portion on acidification with dilute hydrochloric acid yielded a solid, which was extracted with ether. The ethereal solution containing the acid part was

* *In earlier communication[35], melting point of odolactone were erroneous due to inadvertent oversight. All the lactones isolated from* G. odorata *had mp* $> 320^{\circ}$.

washed with water till neutral and dried. The solvent distilled off to yield a residue which constituted the acid part of the extract.

Homogeneity of odolactone

It gave a single spot on TLC Fluka plate of silica gel (F_{254}) with benzene-ethyl acetate (9:1) as the eluent. The spot was stained by spraying acetic anhydried-sulphuric acid mixture. Its homogeneity was also evident from its MS (Fig 1) that showed a single molecular ion peak at m/z 454 and from ^{13}C NMR (Fig 5) which exhibited 29 sharp peaks.

Some properties of odolactone

Odolactone, mp>320°, is levorotatory, $[\alpha]_D$ -47.06°. It is soluble in chloroform, ethyl acetate, benzene, moderately soluble in ether but sparingly soluble in methanol and insoluble in water. It is neutral to litmus. It is insoluble in either dilute hydrochloric acid or sodium hydroxide solution. It is stable in methanolic potassium hydroxide even in refluxing condition.

The chloroform solution of the compound produced light pink coluration with acetic anhydride-sulphuric acid mixture (Liebermann-Burchardt test for triterpenoids) and did not developed yellow colouration with tetranitromethane showing the absence of carbon — carbon double bond.

SECTION B

SPECTROMETRIC ANALYSIS OF ODOLACTONE

IR spectrum of odolactone

The IR spectrum (Fig 2) of odolactone was examined in potassium bromide disc with nujol mulling. The important peaks and their assignment are recorded in Table 1.

Table 1

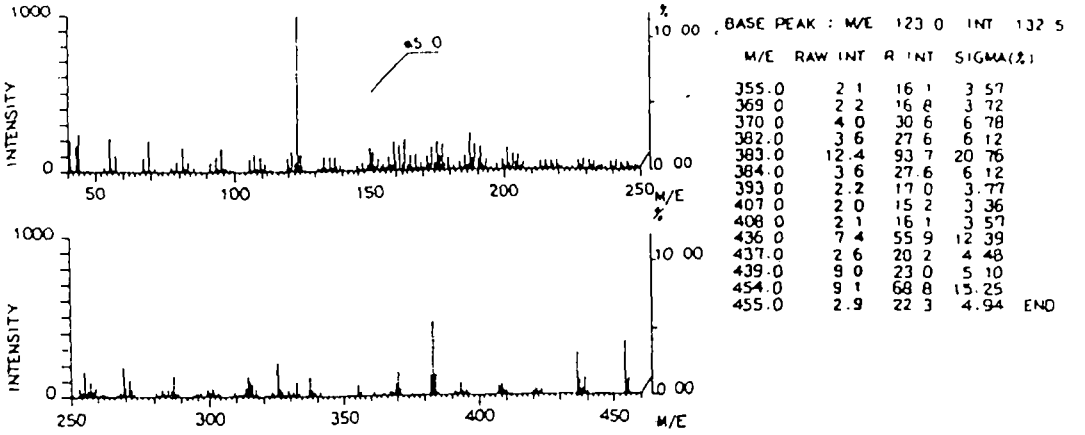
IR absorption peaks of odolactone

Position of the peaks	Probable assignment
1710 cm^{-1}	C = O stretching of a 6-membered ring ketone
1755 cm^{-1}	C = O stretching of a γ-lactone ring

The peaks at 1755 cm^{-1} indicated the presence of a γ-lactone moiety and the one at 1710 cm^{-1} showed the presence of a ketone moiety.

CD spectrum of odolactone

The CD spectrum of odolactone in methanol with a few drops of chloroform is shown in Fig 3. It shows a negative



BASE PEAK : M/E 123.0 INT 132.5

M/E	RAW INT	R INT	SIGMA(%)	
355.0	2.1	16.1	3.57	
369.0	2.2	16.8	3.72	
370.0	4.0	30.6	6.78	
382.0	3.6	27.6	6.12	
383.0	12.4	93.7	20.76	
384.0	3.6	27.6	6.12	
393.0	2.2	17.0	3.77	
407.0	2.0	15.2	3.36	
408.0	2.1	16.1	3.57	
436.0	7.4	55.9	12.39	
437.0	2.6	20.2	4.48	
439.0	9.0	23.0	5.10	
454.0	9.1	68.8	15.25	
455.0	2.9	22.3	4.94	END

Fig 1. MS spectrum of odolactone (37)

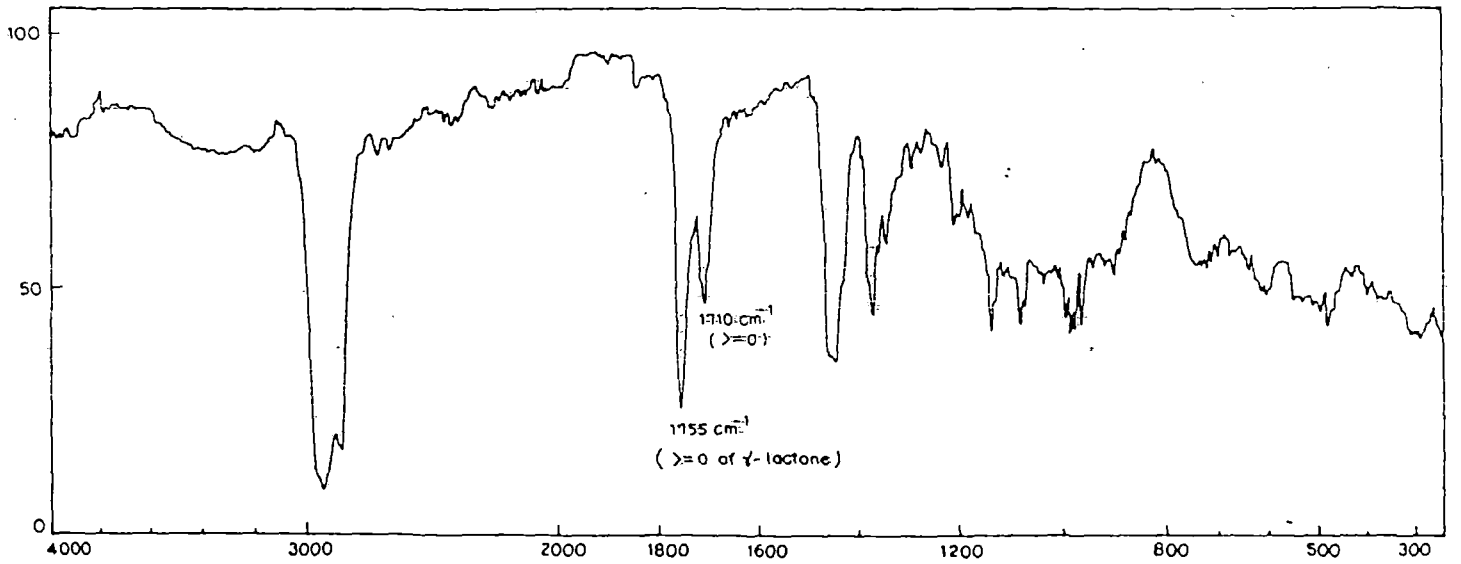


Fig 2. IR spectrum of odolactone (37)

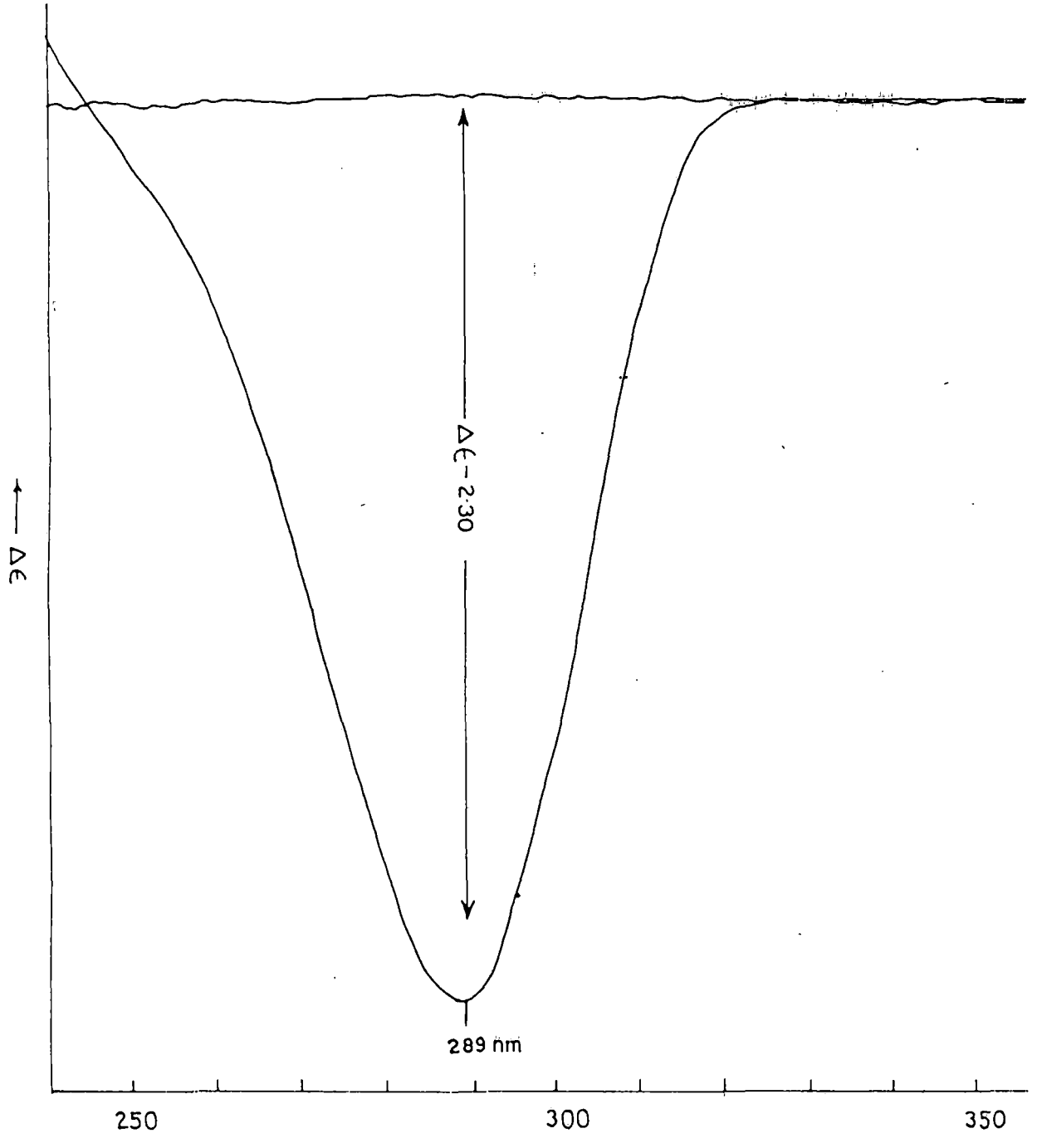


Fig 3. CD spectrum of odolactone (37) in MeOH – $CHCl_3$

Cotton effect with $\Delta\epsilon$ -2.30 at 289 nm.

^{1}H NMR spectrum of odolactone

The ^{1}H NMR spectrum of odolactone at 300 MHz is shown in Fig 4. Fig 4a is the plot expansion of the upfield region with integration curves. Singlets at 0.73, 0.88, 0.96, 0.98, 1.02 and 1.16 ppm for six tertiary methyl groups, doublet at 0.87 ppm (J = 6.5 Hz) for a secondary methyl, multiplets centred at 2.27 and 2.40 ppm for two and one protons respectively, and a triplet at 4.38 ppm (J = 3 Hz) for a single proton, are the major important peaks of ^{1}H NMR of odolactone. The observed chemical shifts, their multiplicities and the functional nature are enumerated in Table 2.

Table 2

^{1}H NMR signals of odolactone

Chemical shifts (ppm)	Number of protons	Multiplicity	Functional nature of protons
0.73	3	Singlet	Tertiary methyl group
0.87	"	Doublet (J = 6.5 Hz)	Secondary methyl group
0.88	"	Singlet	Tertiary methyl group
0.96	"	"	"
0.98	"	"	"
1.02	"	"	"
1.03	1	Broad	Methine proton
1.16	3	Singlet	Tertiary methyl group
1.20-2.10	20	Multiplet	Saturated methylene and methine protons
2.27	2	Multiplet	A methylene and a methine protons, alpha to Keto group

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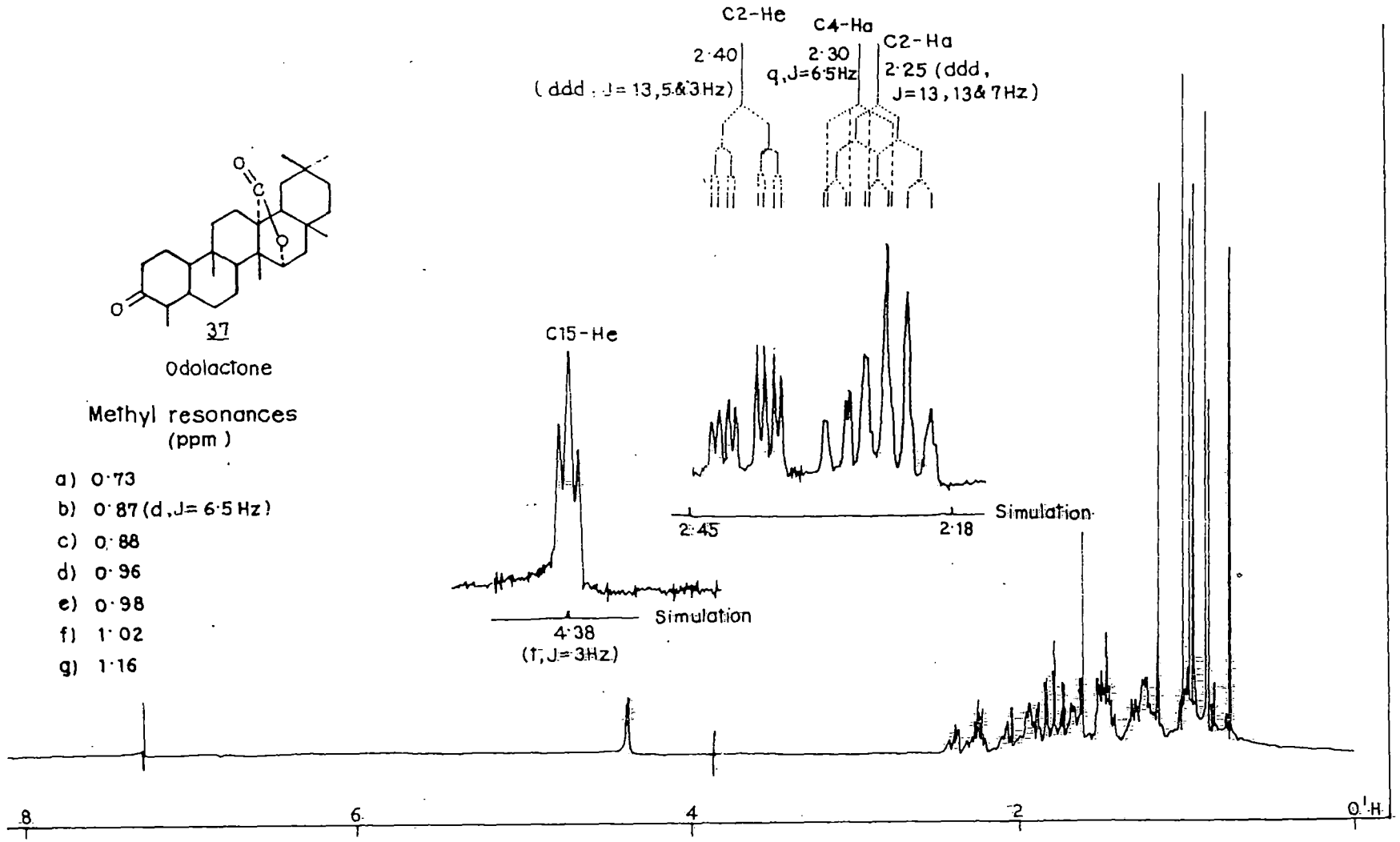

Fig 4. ^{1}H NMR spectrum of odolactone (37) at 300 MHz

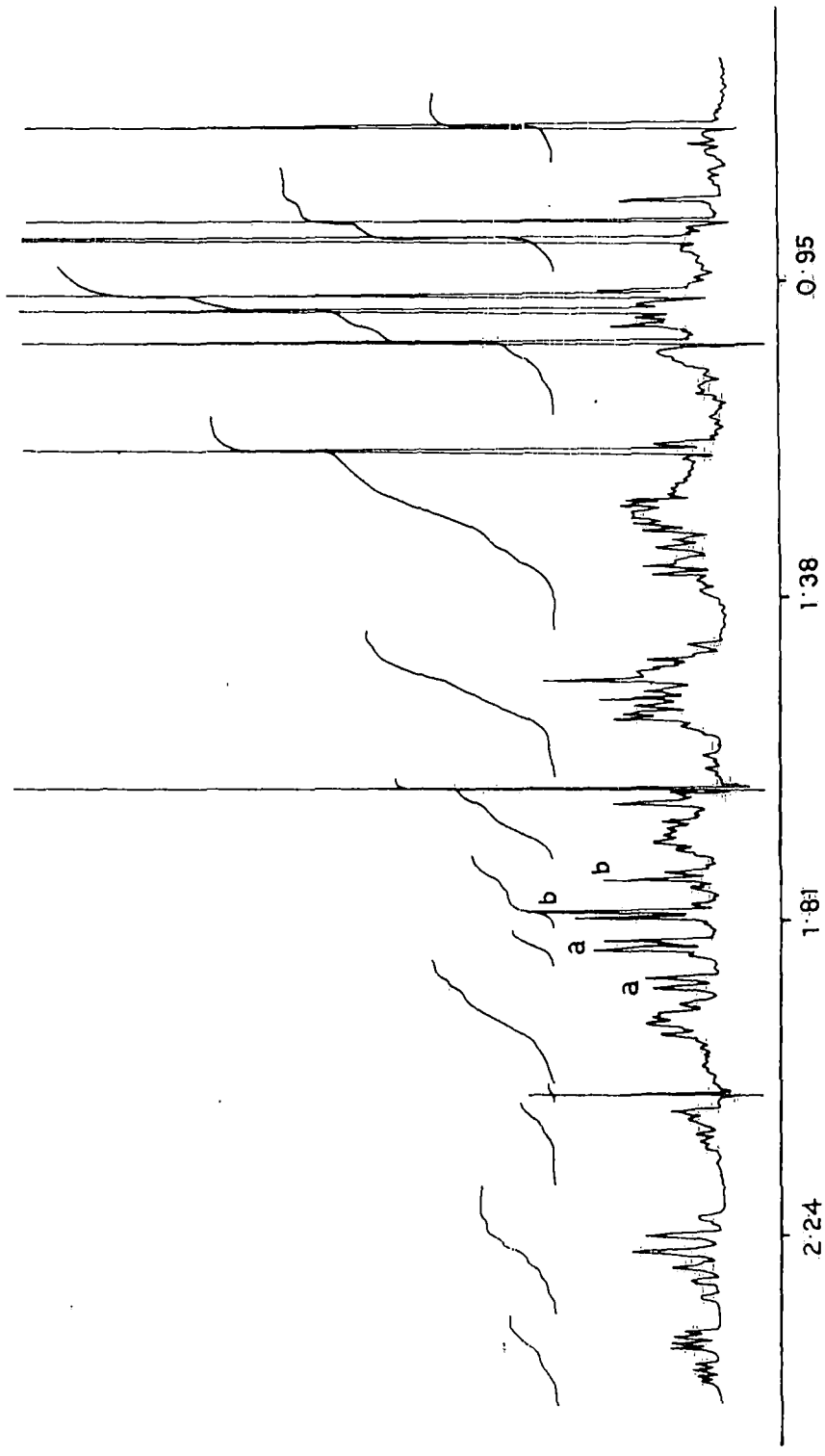

Fig. 4a. Plot expansion of Fig. 4.

Table 2 (continued)

Chemical shifts (ppm)	Number of protons	Multiplicity	Functional nature of protons
2.40	1	Multiplet	A methylene proton, alpha Keto group
4.38	1	Triplet (J = 3 Hz)	A methine proton, geminal to lactone oxygen

Total no. of protons = 46

Thus the presence of the following structural features in the molecule is revealed :

i) six tertiary and one secondary methyl groups
ii) one methylene group alpha to the keto group
iii) one methine group alpha to the keto group
and iv) a methine proton attached to a carbon bearing the lactone oxygen.

^{13}C NMR spectrum of odolactone

The ^{13}C NMR spectrum of odolactone at 75 MHz is shown in Fig 5. A total of 29 peaks (exclusive of $CDCl_3$) are found, one of which at 34.27 ppm represents two carbons, making a total of 30 carbons; two of them are for carbonyl peaks, one at 212.53 ppm (for a ketone carbon) and the other at 180.07 ppm (for a lactone carbonyl carbon).

Fig 6 is the result of APT[27] pulse sequence in which the CH_3 and CH peaks are reversed in phase and point down, while CH_2 and non-protonated carbons are positive. There are nine strong positive peaks (marked with circles) due to $9CH_2$, six weak positive peaks for 6 non-protonated carbons, six weak negative peaks (marked with X letters) for $6CH_3$ and five strong negative peaks for 5 CH carbons. The peak at 34.27 ppm (marked with Y) which represents two

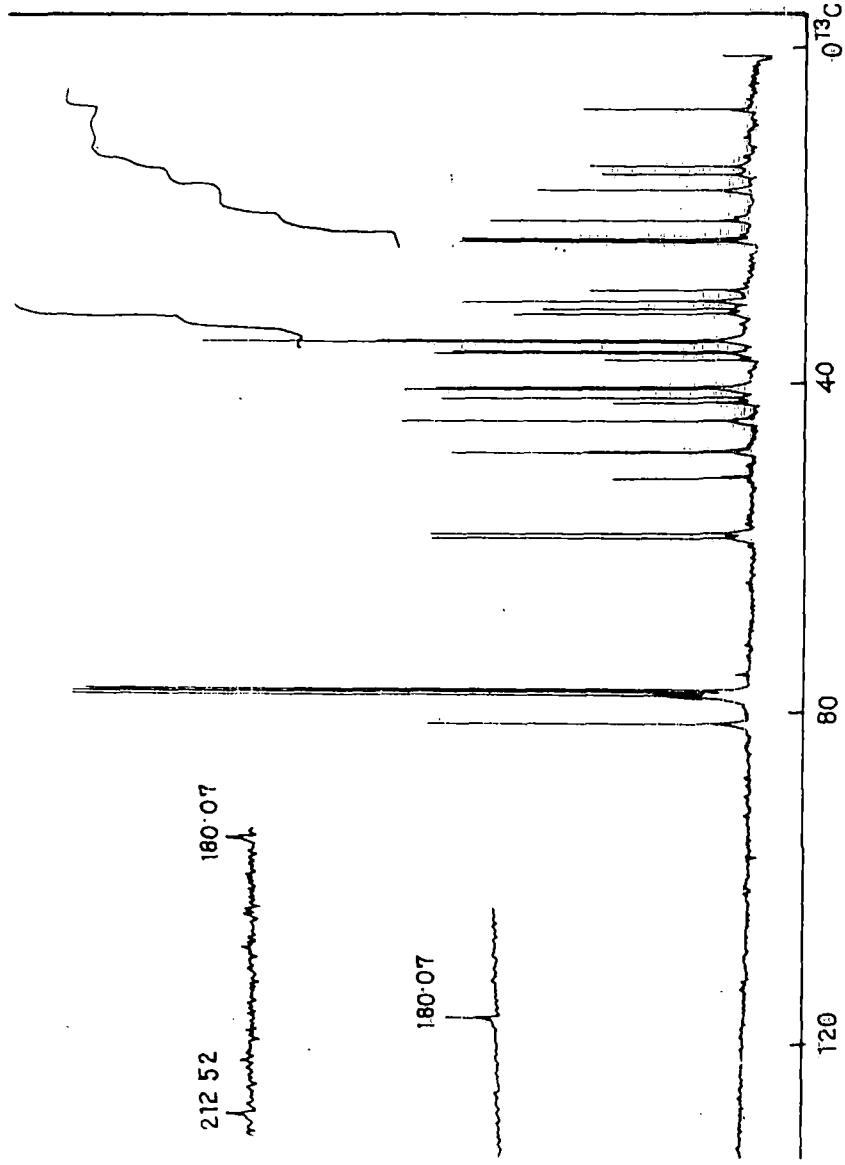

Fig 5. ^{13}C NMR spectrum of odolactone (37) at 75 MHz

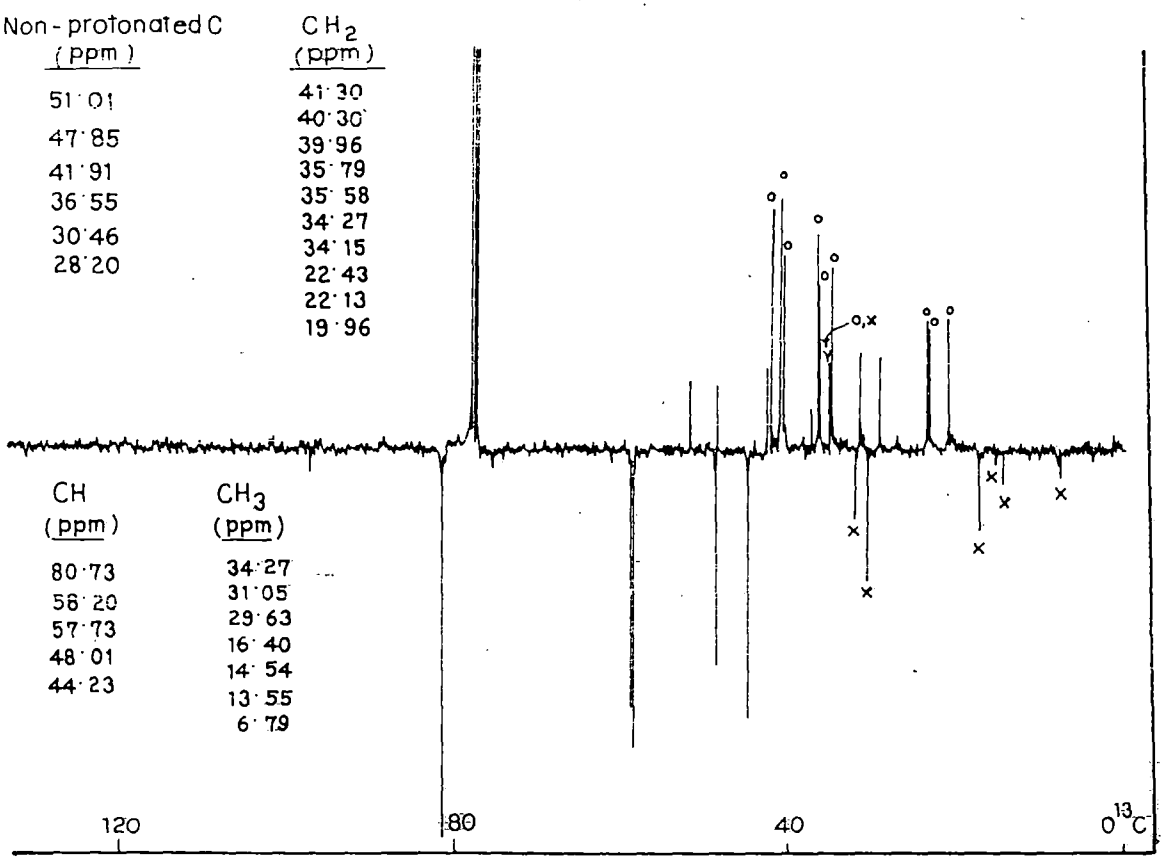

Fig 6. APT Spectrum of odolactone (37) at 75 MHz

carbons in normal spectrum, is quite small in the APT spectrum and this is explained by a superposition of negative peak for a methyl group (the 7th methyl) and a strong positive peak for a CH_2 group (the 10th methylene) resulting in the appearance of a diminished single peak for two carbons. Similar results were obtained from DEPT ^{13}C NMR spectral editing[28] (Fig 7). Carbon-13 chemical shift values of different groups of odolactone are shown in Table 3.

Table 3

Carbon-13 chemical shifts of different groups present in odolactone

Groups	Number of groups	Carbon-13 chemical shifts (ppm)
$-CH_3$	7	6.79, 13.55, 14.54, 16.40, 29.63, 31.05, 34.27
$-CH_2$	10	19.96, 22.13, 22.43, 34.15, 34.27, 35.58, 35.79, 39.96, 40.30, 41.30
$-CH$	4	44.23, 48.01, 57.73, 58.20
O-CH (diagnosed from shift value)	1	80.73
$-C-$	6	28.20, 30.46, 36.55, 41.91, 47.85, 51.01
$-C=O$	2	180.07, 212.53

Total number of carbons = 30, protons = 46, oxygen = 3

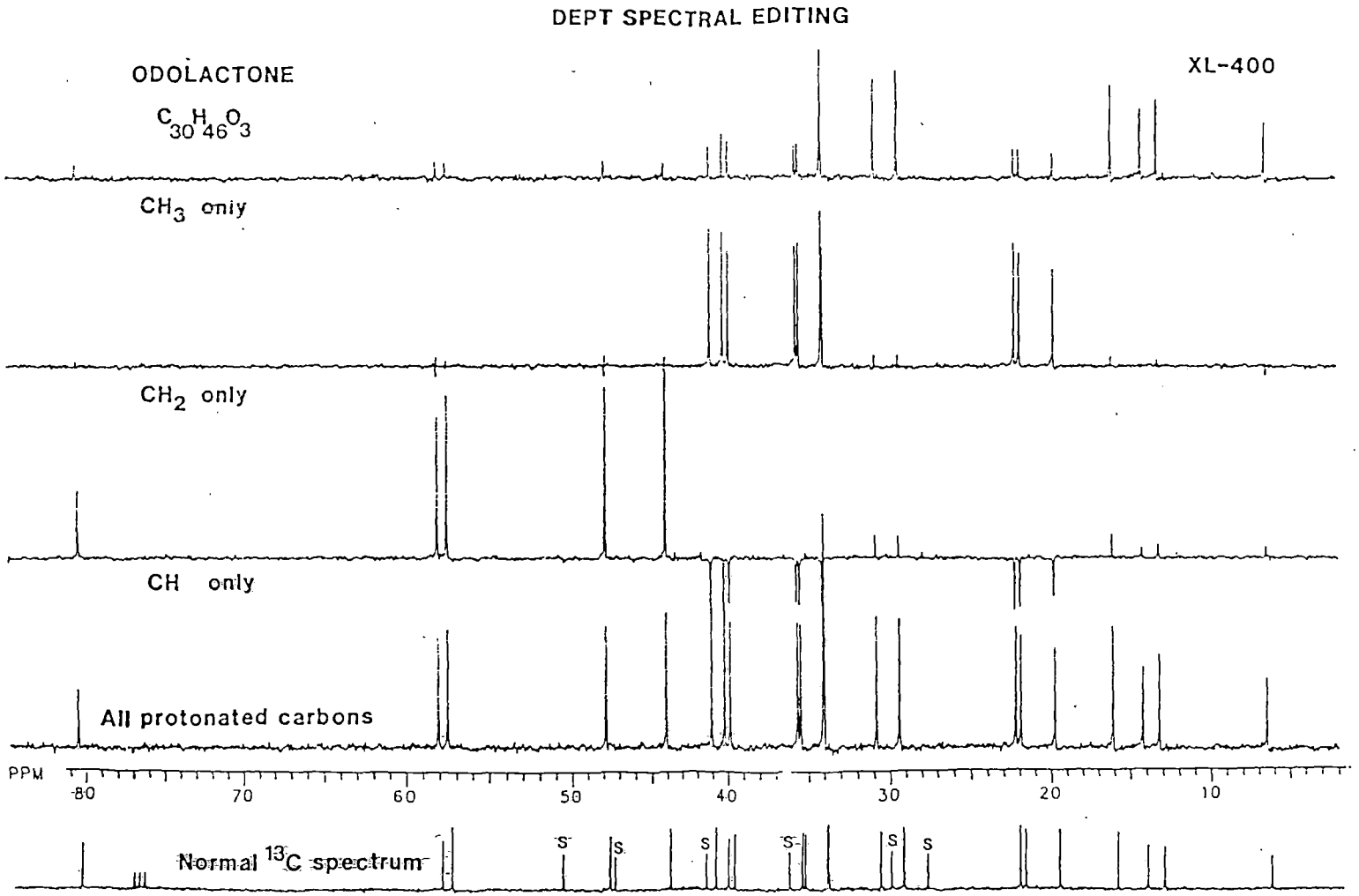

Fig 7. DEPT editing ^{13}C spectrum of odolactone (37)

SECTION C
THE STRUCTURE OF ODOLACTONE

Molecular formula of odolactone — functional nature of oxygens

The IR showed the presence of a 6 membered keto group and a γ-lactone moiety (Table 1) accounting for the presence of at least three oxygen atoms in odolactone. The ^{1}H NMR accounted for 46 protons (Table 2), and ^{13}C NMR for 30 carbons, 46 protons and three oxygens (Table 3). All these corroborate the molecular formula of odolactone as $C_{30}H_{46}O_3$ which is confirmed by the appearance of molecular ion at M^+ 454 in MS (Fig 1) and from elemental analysis. The functional nature of the oxygen atoms is also established.

Carbon skeleton of odolactone

Replacement of three oxygen atoms of odolactone (mf $C_{30}H_{46}O_3$) by six monovalent hydrogen atoms would furnish the parent hydrocarbon of molecular formula $C_{30}H_{52}$ for which the double bond equivalent[29] is $\frac{1}{2}(30 \times 2 + 2 - 52) = 5$. Since odolactone does not contain carbon-carbon double bond, it must be pentacyclic, i e, odolactone belongs to the class of pentacyclic triterpenoids.

Odolactone contains $7CH_3$, $10CH_2$, 5CH and eight quaternary carbons as evident from APT and DEPT experiments (Fig 6 & 7). The ^1H NMR (Fig 4a) shows that one of the seven methyl groups is a secondary methyl, CH_3 — CH. The remaining six are tertiary. These functionalities could well be fitted with the skeleton of friedelane (6). In friedelane, there are $8CH_3$ (one of them is secondary), $12CH_2$, 4CH and six quarternary carbons. In odolactone, one of the tertiary methyl groups of friedelane has been converted to the lactone carbonyl carbon, one of the CH_2 groups is attached to the lactone oxygen making it a methine group and another CH_2 has been converted to the ketone carbonyl carbon; thus accounting for the 8-1 = $7CH_3$, 12-2 = $10CH_2$, 4+1 = 5CH and 6+2 = 8 quarternary carbons in the molecule.

Position of the keto group in odolactone

The peaks centred at 2.40 and 2.27 ppm in ^1H NMR spectrum (Fig 4a) of odolactone represent one and two protons respectively as evident from the integration curves. These protons are attached to carbons, alpha to the keto group, because they disappeared when the keto group was reduced by $NaBH_4$. The following discussion suggests that the keto group is at C-3 position.

The equatorial proton on C-2 appeared downfield at 2.40 ppm and is coupled with the axial proton at C-2 with the coupling constant, J = 13 Hz which is further coupled with an axial and equatorial protons on C-1 with J = 5 Hz and J = 3 Hz (this low coupling constant often results due to the distortion of ring-A) resulting two quartets of a doublet. The axial proton on C-2 appeared at 2.25 ppm and is coupled with the equatorial proton on C-2 with the geminal coupling constant, J = 13 Hz which is further coupled with an axial and equatorial protons on C-1 with J = 13 Hz (a/a coupling) and J = 7 Hz (a/e coupling) resulting a sextet. The axial proton on C-4 appeared at 2.30 ppm

is a quartet due to the coupling with methyl protons on C-23 with the same coupling constant (J = 6.5 Hz) as the C-23 methyl gives a doublet. The splitting patterns of these protons are shown schematically on Fig 4.

Alternative possibilities still remained to fix the Keto group either at C-1 or at C-7 which might satisfy the appearance of three protons attached to carbons, alpha to the Keto group. But such types of assignment could not explain the observed splitting patterns; these would result one of the methine protons (ie, C10-H or C8-H) around 2-3 ppm as singlet.

The position of the keto group at C-3 is further supported from the fact that CD spectrum of odolactone (Fig 3; $\Delta\epsilon$ - 2.30 at 289 nm in $MeOH/CHCl_3$) is comperable with that of friedelin, 26 ($\Delta\epsilon$ - 2.69 at 290 nm in dioxan*). The 3-keto compounds with trans fused A/B ring juncture with gem-dimethyl at C-4 (like lupanone) are invariably show positive Cotton effect whereas those with similar ring disposition with a secondary methyl group at C-4 (like friedelin) show negative Cotton effect**.

Position of lactone carbonyl carbon and lactone oxygen attachment in odolactone

The assignment of the ^1H NMR methyl chemical shifts of odolactone (Table 2) might lead to the identification of the position of lactone carbonyl carbon. This may be achieved by comparing with those of friedelin (26) as shown in Table 5.

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* The value is kindly supplied by Dr S N Bose, Reader, Department of Chemistry, University of North Bengal, Darjeeling, India.

** Crabbe P, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry", Holden-Day, London (1965).

Table 4[31]

Methyl chemical shifts (ppm) in ^{1}H NMR of some friedelane derivatives

	Methyl groups							
	23*	24	25	26**	27**	28	29	30
Friedelin (26)	0.87	0.72	0.86	0.99	1.04	1.16	0.94	0.99
Canophyllal (27)	0.87	0.71	0.84	0.96	1.06	-	0.94	0.67
Canophyllol acetate (28)	0.87	0.72	0.88	0.99	1.12	-	0.95	0.99
Methylfriedelan-3-one-28-oate (29)	0.87	0.72	0.84	1.04	1.04	-	0.93	0.72
Friedelan-3-one-25-al (30)	0.90	0.63	-	0.94	1.05	1.14	0.94	0.94
25-Acetoxy-friedelan-3-one (31)	0.90	0.76	-	1.08	1.02	1.18	0.96	0.99

* Doublets J = 6-8 Hz
** Methyl shifts may have to be interchanged

The methyl chemical shifts of friedelin have been assigned (Table 4) by Crawford et al[30] by using the shift reagent, Eu(fod)$_3$. They assigned the chemical shifts for C-23, C-24 and C-25 methyl definitely. Considering the methyl shifts of some canophyllal derivatives and 25-oxy-friedelin derivatives (Table 4), Anjaneyulu et al[31] supported the assignment made by Crawford et al as well as confirmed the chemical shift for C-28 methyl protons. The possibility of interchange in the shifts of C-26 and C-27

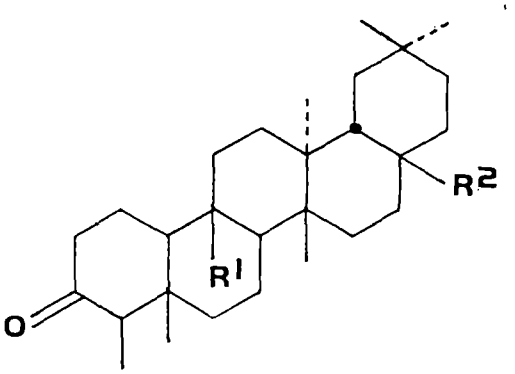
Table 5

Comparison of ^1H NMR methyl chemical shifts of odolactone and friedelin (26)

Methyl chemical shifts in ppm		
Odolactone	Friedelin*	Assignment
0.73	0.72	C-24
0.87(d)	0.87(d)	C-23
0.88	0.86	C-25
0.96	0.94	C-29
0.98	0.99	C-30
1.02	1.04	C-27+ or C-26
1.16	1.18	C-28

* From Table 4

+ Most likely assignment



26 $R^1 = R^2 = CH_3$

27 $R^1 = CH_3$, $R^2 = CHO$

28 $R^1 = CH_3$, $R^2 = CH_2OAC$

29 $R^1 = CH_3$, $R^2 = COOCH_3$

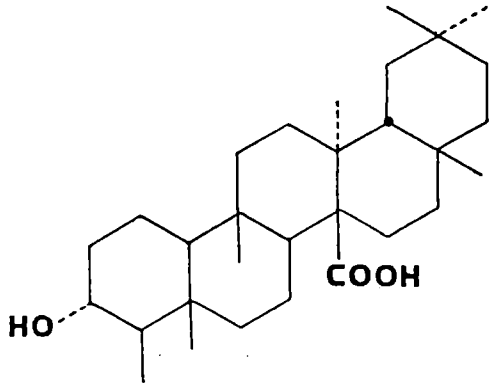
30 $R^1 = CHO$, $R^2 = CH_3$

31 $R^1 = CH_2OAc$, $R^2 = CH_3$

methyls, as proposed by Crawford et al, remained unsolved. However, the shift at 1.02 ppm of odolactone, based on explanation offered by Anjaneyullu, may be presumed to be due to C-27 methyl which left the position C-26 for lactone carbonyl carbon as the only alternative. It is to be noted that the shift at 0.88 ppm (assigned for C-30 methyl, Table 5) is also comparable with that of C-26 methyl of friedelin (cf 0.99 ppm, Table 4) which reflects the possibility for the location of lactone carbonyl carbon at C-30. The last argument is ruled out as it would influence the chemical shifts of C-29 and C-28 methyls otherwise[31,32]. However, the position of lactone carbonyl carbon at C-26 is confirmed by converting odolactone to trichadenic acid A, which is believed to have the structure 32[33], with the help of lithium in ethylenediamine under nitrogen atmosphere.

Since odolactone contains a 5-membered lactone moiety (evident from IR), it might have one of the four possible structures, 33, 34, 35 or 36.

The ^{1}H NMR peak at 4.38 ppm is simulated to be a triplet with $J = 3$ Hz (Fig 4). This is attributed to a single proton attached to the carbon bearing the lactone oxygen. The low coupling constant suggests that the proton is equatorial that has only one axial and one equatorial neighbouring protons, the lactone oxygen being axial. This determines the stereochemistry of the lactone oxygen as well as rules out the structures 35 and 36. The peaks due to protons adjacent to lactone oxygen are marked with letters 'a' and 'b' on Fig 4a. Each proton (1.85 & 1.76 ppm) appeared as quartets owing to geminal coupling (J = 15 Hz) with each other and vicinal coupling ($J = 3$ Hz) with the equatorial proton on the carbon bearing the lactone oxygen. The peaks are slightly broadened. The broadening of the peaks may be due to the coupling with the nearby axial C-25 methyl protons and hence the structure 33 for



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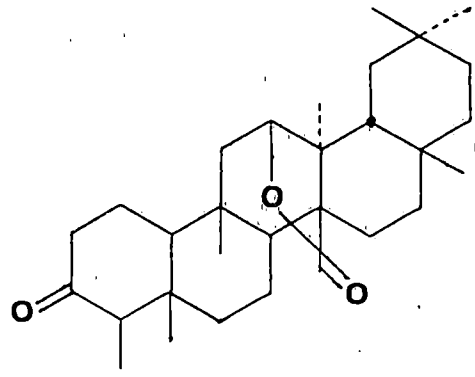

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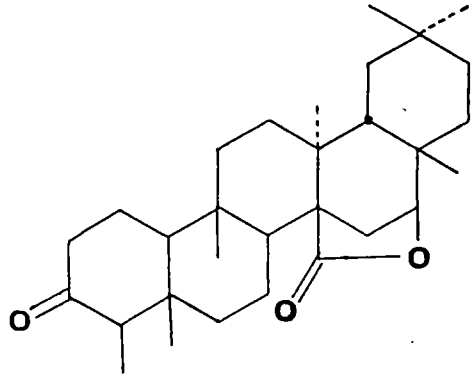

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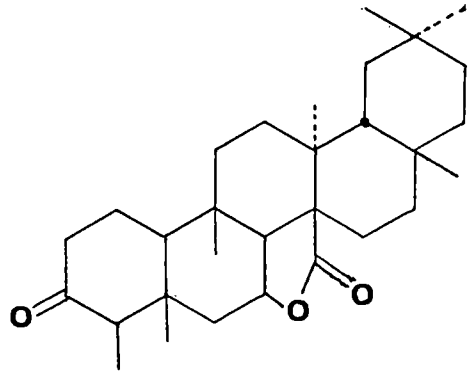

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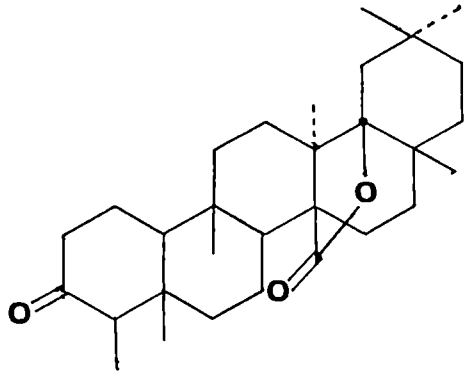

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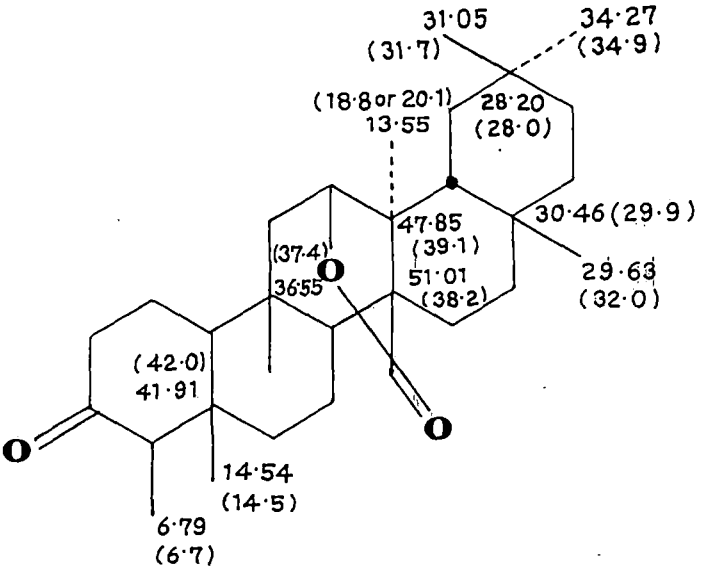
odolactone is more favoured.

Finally, it is observed that the ^{13}C chemical shifts of the methyl and quarternary carbons of odolactone as 3-oxofriedelan-26→12β-olide (33) agree well with those for friedelin (26) as shown in the following :



[Data in parenthesis are ^{13}C chemical shifts of respective carbons of friedelin and were those assigned by Patra et al[34]]

There are reasonable downfield shifts of C-13 and C-14 and upfield shift of C-27 signals. If 34 is taken as the structure of odolactone, there should be downfield shift for C-17 by greater than 5 ppm and upfield shift for C-28 by about 5 ppm and the signal for C-27 would appear around 18 ppm.

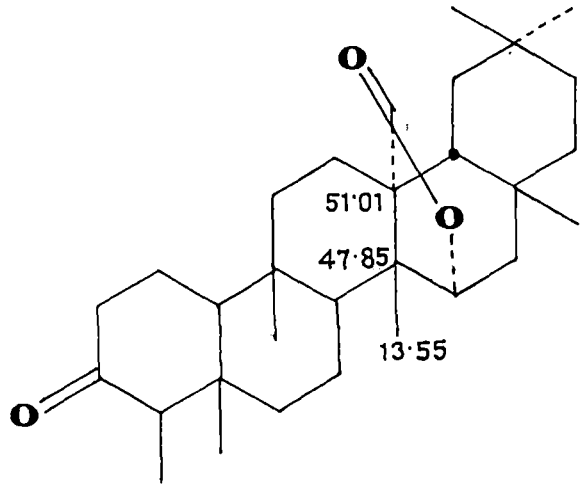
The result of the above discussion, which established the structure of odolactone as 3-oxofriedelan-26→12β-olide (33) was reported[35].

SECTION D

APPLICATION OF 2D NMR TECHNIQUES ON ODOLACTONE REVISION OF THE PREVIOUS STRUCTURE OF ODOLACTONE AND SOME OTHER NATURALLY OCCURRING TRITERPENOIDS OF THE FRIEDELANE GROUP

Some questions about the correctness of the structure 33 for odolactone have arisen on thorough re-examination of the previous arguments. The position of the lactone carbonyl carbon at C-26, in the previous section was established by assigning its methyl chemical shifts of ^{1}H NMR by comparing with those of friedelin (26) and transforming it to trichadenic acid A. The termination point of lactone oxygen at C-12 was established by interpreting some selective ^{1}H NMR peaks of interest (marked by 'a' and 'b' letters on Fig 4a). Finally, the structure was confirmed by correlating ^{13}C signals for methyl and quarternary carbons of odolactone with those of friedelin. It has already been pointed out that the ^{1}H NMR shifts for C-26 and C-27 methyls of friedelin may be interchangeable (Table 4). Therefore, the signal at 1.02 ppm of odolactone could be assigned for C-26 methyl protons (noted in Table 5), and so C-27 may be the lactone carbonyl carbon. Moreover, in determining the structure of trichadenic acid A and its derivatives, Sultanbawa et al[33] seemed to have

rightly limited the position of the carboxylic carbonyl at C-26 or C-27, but they favoured the position C-26 without giving evidence, neither physical nor chemical, in favour of it. Further, the ^{13}C shifts of methyl and quarternary carbons of odolactone could appropriately be accommodated in the structure 37, for which the methyl signal at 13.55 ppm could be explained as due to C-26 and the singlet peaks at 51.01 and 47.85 ppm are those for C-13 and C-14 respectively.



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The most promising avenue of approach to the problem appears to be the use two-dimensional NMR techniques, which has been recognized as a powerful and reliable tool in structural studies of organic molecules. These modern techniques are now applied routinely in all those cases where conventional spectral interpretation lead to an ambiguous results. There are several versions of 2D NMR[36]. Here, two techniques, firstly 2D COSY and finally CCC 2D have been applied. It served the purpose uniquely.

Two-dimensional proton homonuclear correlation spectroscopy (2D COSY) of odolactone

A contour plot of 2D COSY[37] of odolactone at 300 MHz is shown in Fig 8 along with the conventional ^{1}H spectrum

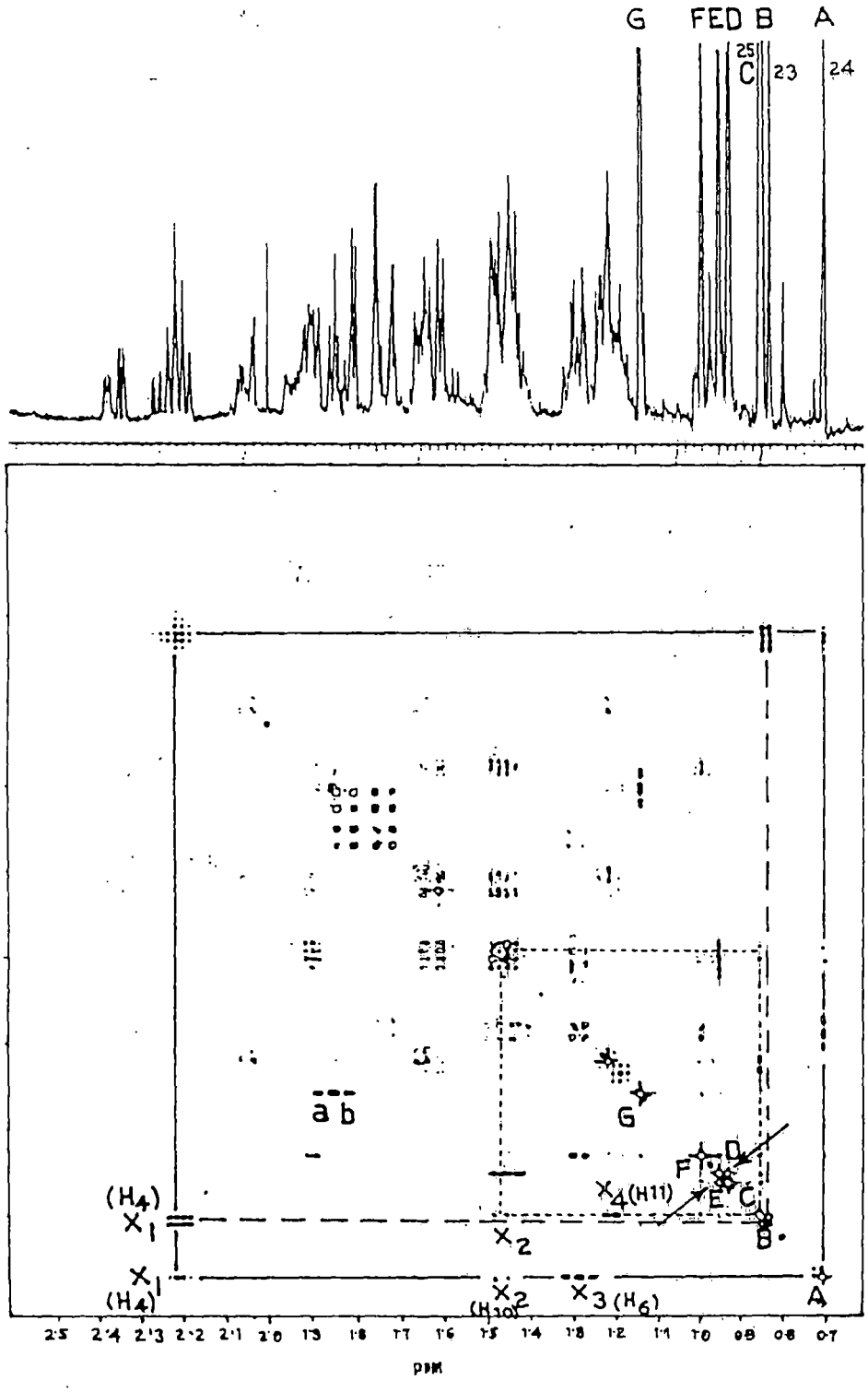


Fig. 8. 2D COSY spectrum of odolactone (3[7])

at the top. Both dimensions of the plot represent ^1H spectrum, with the spectral peaks falling on the diagonal. Off-diagonal peaks appear in symmetrical positions and denote coupling between the two protons represented by the peaks at the corresponding positions on the diagonal. This plot shows that the methyl (B) at 0.87 ppm, a doublet with the vicinal coupling constant J = 6.5 Hz, is correlated (shown by broken line) to a proton (x_1 signals) which is quartet with J = 6.5 Hz, and no other protons. This is obviously due to the C-23 methyl which undergoes vicinal coupling with the proton on C-4. The methyl (A) at 0.73 ppm is correlated (shown by solid line) to the proton on C-4 (x_1 signals) and to two other groups of signals (x_2 and x_3 signals) at $\sim$1.48 and $\sim$1.28 ppm. The proton (x_2 signals) at $\sim$1.48 ppm is, on the other hand, correlated (shown by dotted line) to the methyl (C) at 0.88 ppm which is further correlated with another proton (x_4 signals) at $\sim$1.22 ppm. Therefore, the signal A at 0.73 ppm is due to the C-24 methyl which is coupled with the axial protons on C-10 (x_2 signals) and C-6 (x_3 signals). The signal (C) at 0.88 ppm is due to the C-25 methyl which is coupled with the axial proton on C-10 (x_2 signals) and with another axial proton (x_4 signals), on C-11. The methyls (D and E) at 0.96 and 0.98 ppm, strongly correlated with each other (shown by head on arrows), are the gem-dimethyls C-29 and C-30; one of them (signal E at 0.98 ppm) - the axial one (ie C-30) correlates with one or more protons (marked by circle) on C-19 and C-21. The 'a', 'b' signals, which seemed to be due to CH_2 protons adjacent to the CH bearing the lactone oxygen, are correlated to the methyl (G) at 1.18 ppm, not to the C-25 methyl protons. This methyl at 1.18 ppm was assigned for C-28 in the previous section. From this, it seems that odolactone has the lactone oxygen at C-15 and the lactone carbonyl at C-27 which corresponds to the structure 37. The C-26 methyl (F) is correlated

only to a proton with one large and one small coupling, and this is C8-H (square box).

The absence of correlations of C-28 methyl with C-18 and C-22 protons, which would be correlated with C-19 and C-21 protons respectively in the 2D plot, could not be explained. But the above assignment provides better explanation for 2D COSY of odolactone.

Application of the carbon-carbon connectivity two-dimensional (CCC2D) experiment on odolactone

All most all NMR techniques for structural proof rely heavily on chemical intuition. The carbon-carbon connectivity two-dimensional technique[38] is exceptionally powerful tool in that it places very little reliance on the chemical interpretation of parameters, but provides direct evidence of the carbon skeleton of a molecule and the molecular structure follows under favourable cases. In this technique, the frequency of double quantum coherence is measured in addition to the normal ^{13}C frequencies by the dedicated pulse sequence 'INADEQUATE'[39]. The frequency of double quantum coherence involving two coupled spin system is the sum of their chemical shift frequencies. Therefore, a bond between two carbon atoms is characterized by their common double quantum coherence frequency.

Fig 9 shows a contour plot of a 75 MHz carbon-carbon connectivity 2D (CCC2D) data set for odolactone. The conventional broad band decoupled ^{13}C spectrum is plotted at the top of the chart. Simple inspection of this plot along with the consideration of other spectral features, unambiguously establishes the structure of odolactone as a 3-oxofriedelan-27→15α-olide (37).

The result of the CCC2D plot (Fig 9) is represented graphically as shown in Fig 10. Fig 10 shows the structure (37) of odolactone in which ^{13}C data in ppm of respective

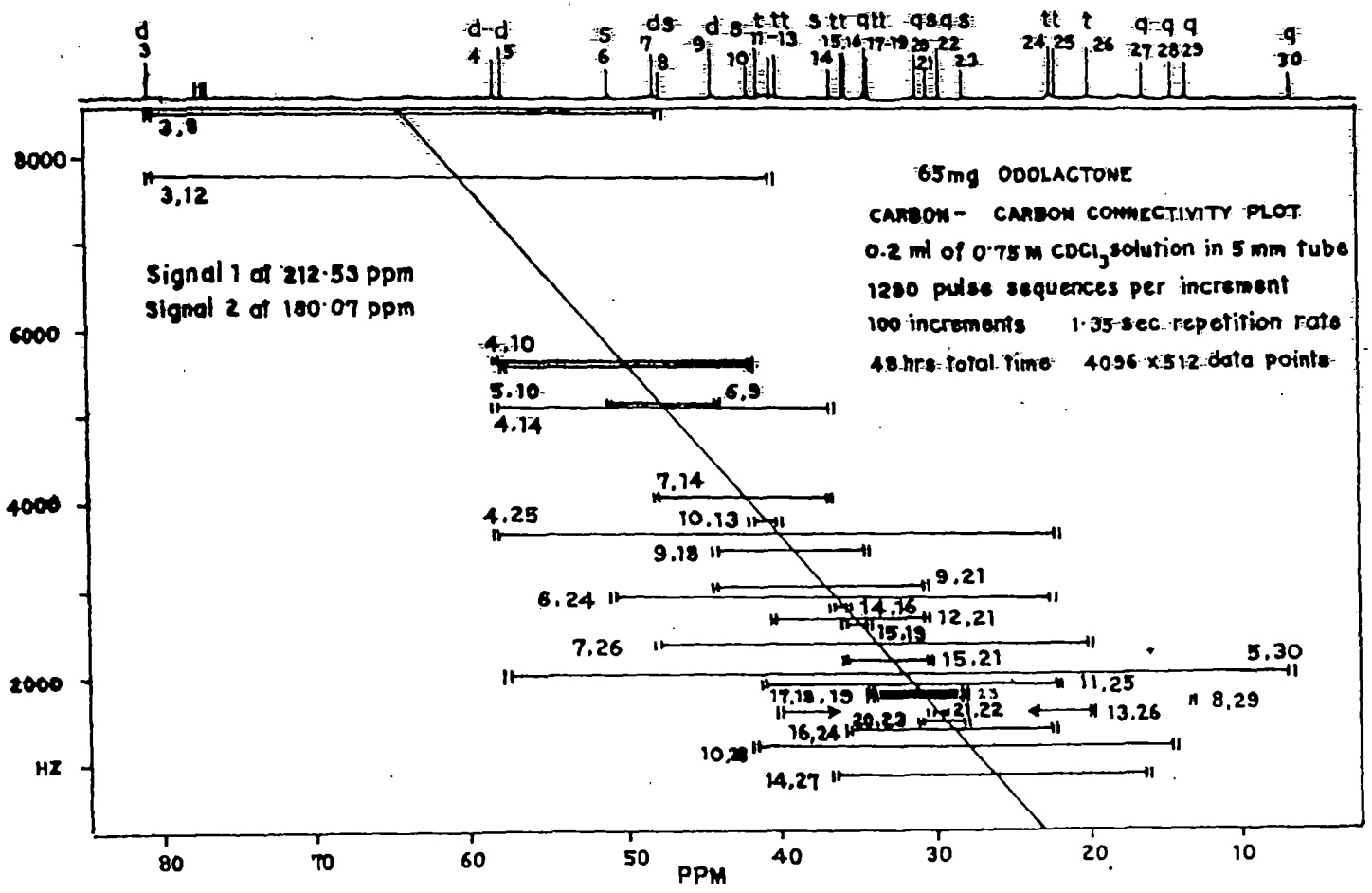


Fig. 9. CCC 2D spectrum of odolactone (37) at 75 MHz

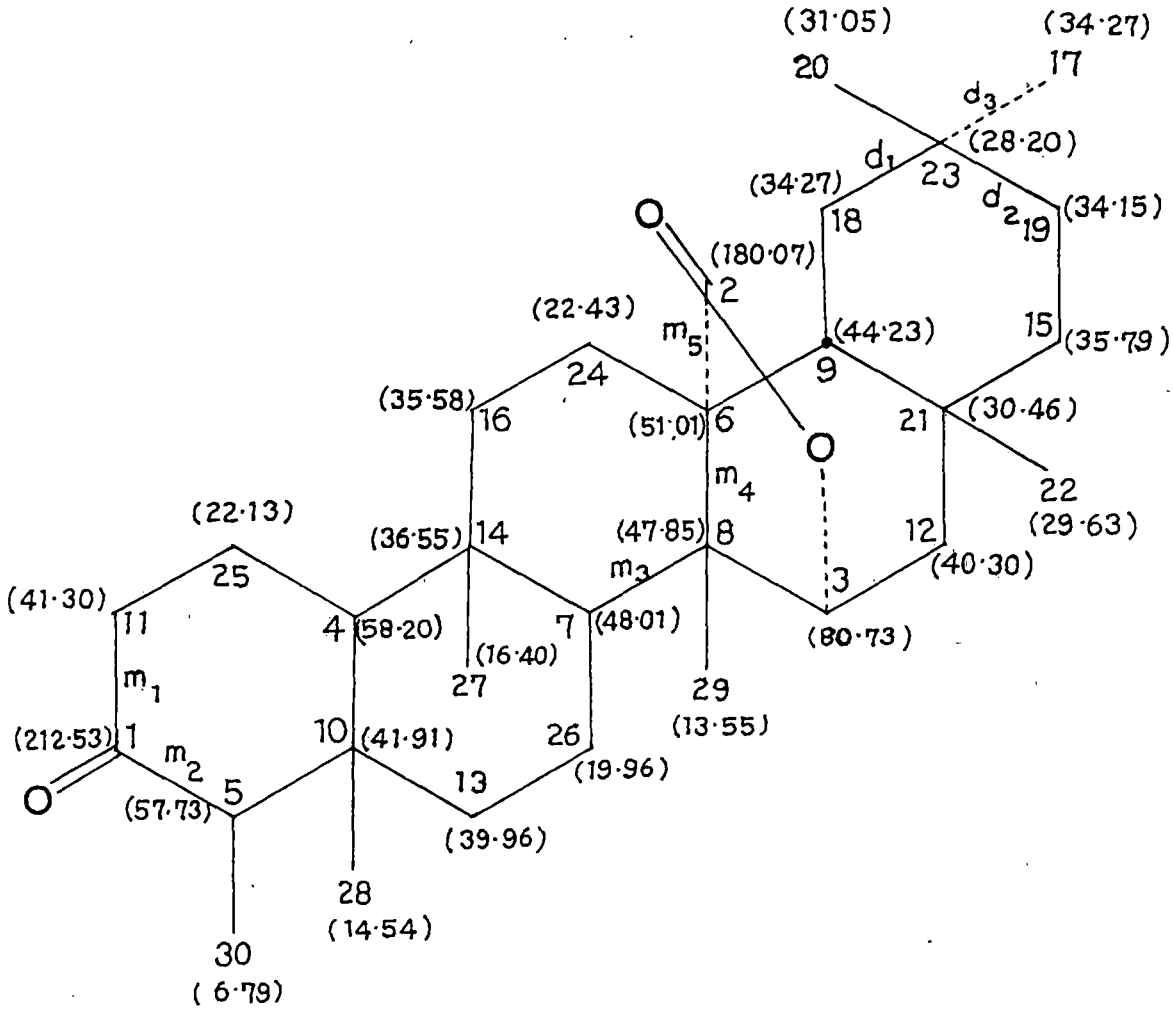
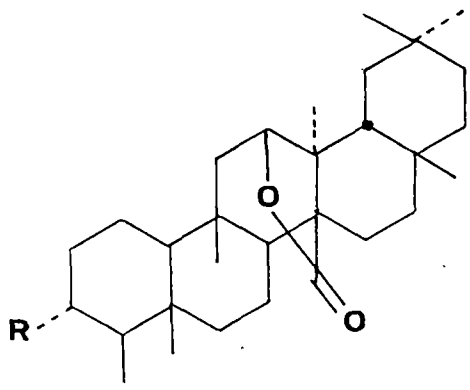


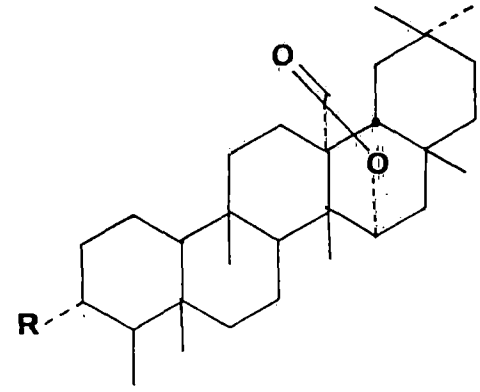
Fig 10. Graphical representation of the result of the CCC2D plot (Fig 9) of odolactone. The numbering system corresponds to a sequential numbering of the signals as they appear in the conventional broad band decoupled ^{13}C spectrum from low to high field. Data in parenthesis are ^{13}C chemical shifts in ppm relative to TMS. The bonds marked by 'm' letters are missing ones and those with 'd' letters are deduced to be represented by superimposed ^{13}C doublets.

carbons are compiled and notes are given, which are not directly derived from the CCC2D plot. The five bonds marked with 'm' letters in Fig 10 are not found in the CCC2D plot because of three different factors : i) long relaxation times for quarternary carbons (missing of m_4 bond), ii) strong coupling due to very close ^{13}C shifts of two coupled sites (missing of m_3 bond) and iii) large chemical shifts of carbonyl carbons resulting in off-resonance effects (missing of m_1, m_2 and m_5 bonds). The connections of signal 1 (212.53 ppm, characteristic signal for ketone carbonyl carbon) to the signals 11 and 5 (ie bonds m_1 and m_2) satisfy their multiplicities and corroborate the ring A of odolactone belonging to the class of friedelane group of triterterpenoid with the oxo group at C-3 (established in the previous section). The bonds m_3 and m_4 corroborate the rings C and D and multiplicities of signals 7 and 8. The multiplicity of signal 6 and its chemical shift (51.01 ppm) suggest the bond m_5 between the carbon with signal 6 and lactone carbonyl carbon (signal 2 at 180.07 ppm). The termination of the lactone oxygen is attributed to C-15 (signal 3), on the basis of its multiplicity and chemical shift (80.73 ppm). The bonds marked with 'd' letters in Fig 10 are indistinguishable in the CCC2D plot. However, they are deduced to arise from the superimposed ^{13}C doublets and the multiplicities of the signals 17, 18, 19 and 23.

The revision of the structure of odolactone as 37 leads to the revision of the structures of its related compounds, isolated from the same source (discussed in the next chapter), namely O-acetylodollactone and odollactone as 40 and 41 respectively. In the earlier communication[35], their structures were reported to be as 38 and 39 respectively.

The naturally occurring triterpenoids, namely trichadenic acid A, O-acetyltrichadenic acid A, O-acetyltrichadenic acid B, trichadonic acid, trichadenal, O-acetyltrichadenal, isolated from Trichadenia zeylanica[33], a



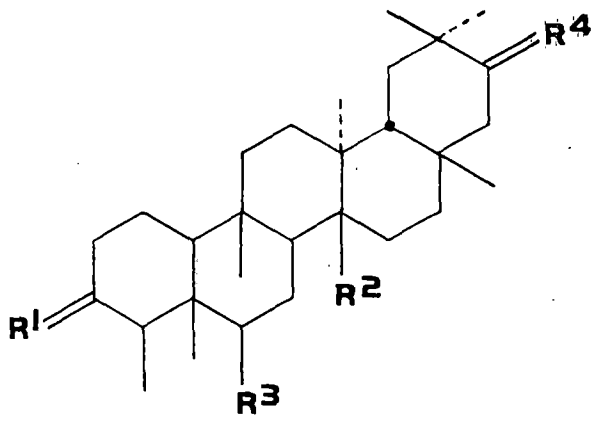


38 R = OAc
39 R = OH

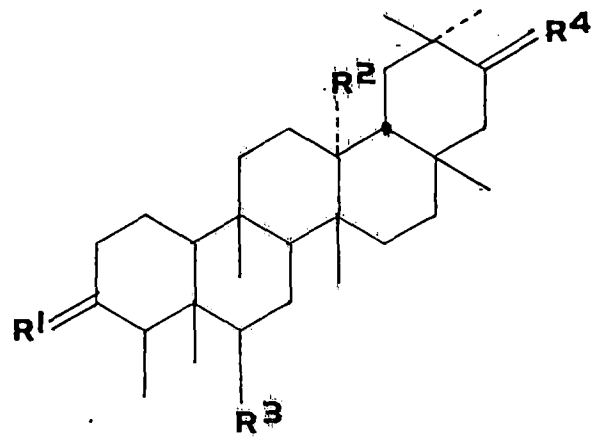
40 R = OAc
41 R = OH

3-oxo-diol from Salacica reticulata[40] and trichademic acid B from Hydnocarpus octandra[55] which are reported to have the structures 42, 42a, 42b, 42c, 42d, 42e, 42f and 42k respectively, are structurally related to odolactone as shown in scheme 1. These structures should be revised to 43, 43a, 43b, 43c, 43d, 43f and 43k respectively. This study also leads to the conclusion that the structures of kokoonol, kokoondiol, kokoononol, kokzeylanol and kokzeylanonol isolated from Kokoona zeylanica[41,42] should be represented as 42g, 42f, 42h, 42i and 42j respectively, instead of 43g, 43f, 43h, 43i and 43j.

Two-dimensional NMR experiments applied to odolactone not only allow the deduction of correct structure of odolactone, but also lead to the revision of a large number of naturally occurring triterpenoids of the friedelane group previously reported, as well as to the unambiguous assignment of ^{13}C chemical shifts of odolactone. Further, they demonstrate the power and usefulness of modern NMR techniques in routine applications to structure elucidation of triterpenoids.

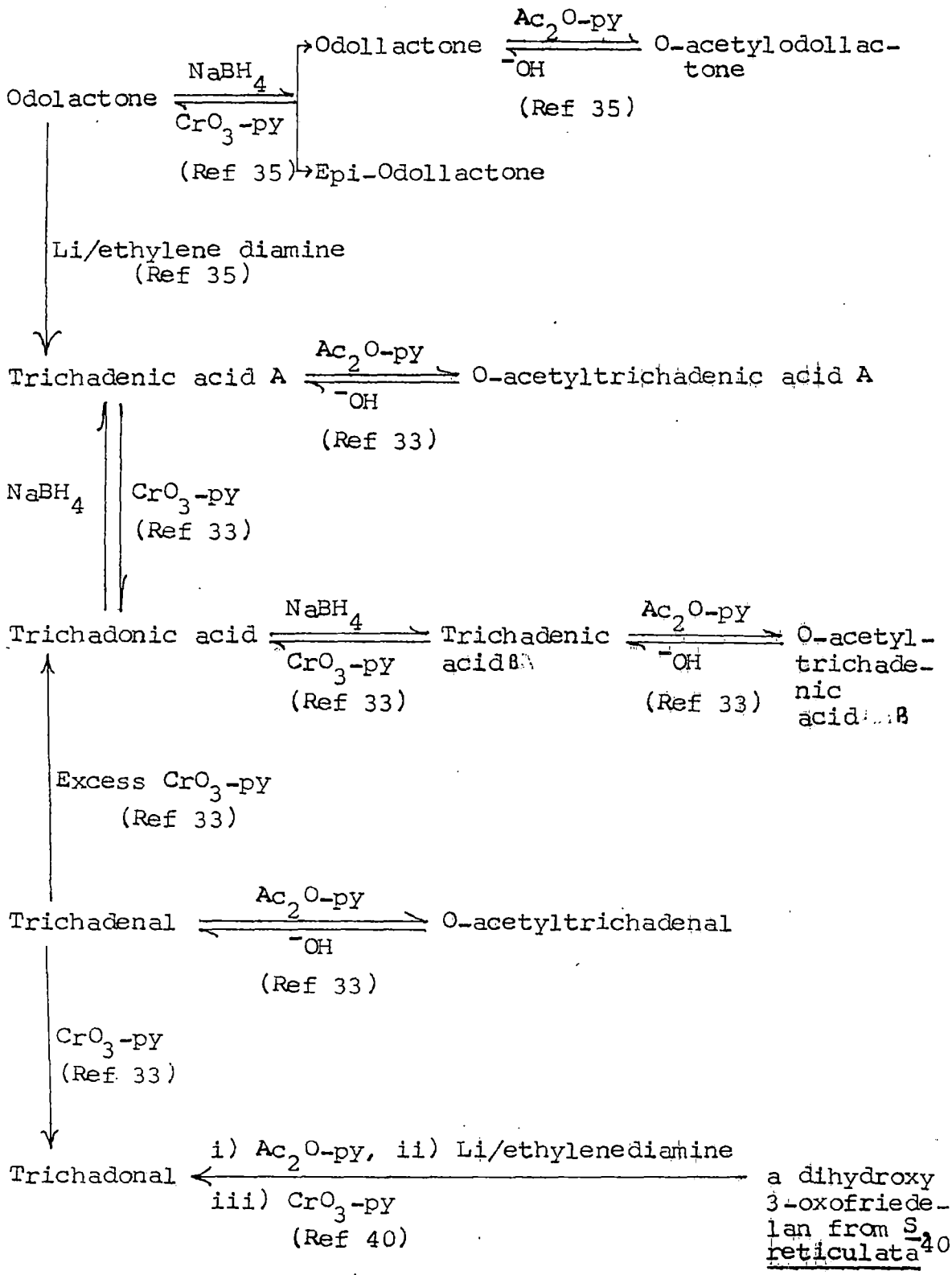


	R^1	R^2	R^3	R^4
42	α-OH, β-H	COOH	H	H_2
42a	α-OAc, β-H	COOH	H	H_2
42b	β-OAc, α-H	COOH	H	H_2
42c	O	COOH	H	H_2
42d	β-OH, α-H	CHO	H	H_2
42e	β-OAc, α-H	CHO	H	H_2
42f	O	CH_2OH	H	OH, H
42g	O	CH_2OH	H	H_2
42h	O	CH_2OH	H	O
42i	O	CH_2OH	OH	H_2
42j	O	CH_2OH	OH	O
42k	β-OH, α-H	COOH	H	H_2



	R^1	R^2	R^3	R^4
43	α-OH, β-H	COOH	H	H_2
43a	α-OAc, β-H	COOH	H	H_2
43b	β-OAc, α-H	COOH	H	H_2
43c	O	COOH	H	H_2
43d	β-OH, α-H	CHO	H	H_2
43e	β-OAc, α-H	CHO	H	H_2
43f	O	CH_2OH	H	OH, H
43g	O	CH_2OH	H	H_2
43h	O	CH_2OH	H	O
43i	O	CH_2OH	OH	H_2
43j	O	CH_2OH	OH	O
43k	β-OH, α-H	COOH	H	H_2

Scheme 1


Odolactone
NaBH4
CrO3-py
(Ref 35)
Odollactone
Epi-Odollactone
Ac2O-py
-OH
(Ref 35)
O-acetylodollactone
Li/ethylene diamine
(Ref 35)
Trichadenic acid A
(Ref 33)
O-acetyltrichadenic acid A
NaBH4
CrO3-py
(Ref 33)
Trichadonic acid
(Ref 33)
Trichadenic acid B
(Ref 33)
O-acetyltrichadenic acid B
Excess CrO3-py
(Ref 33)
Trichadenal
(Ref 33)
O-acetyltrichadenal
CrO3-py
(Ref 33)
Trichadonal
i) Ac2O-py, ii) Li/ethylenediamine
iii) CrO3-py
(Ref 40)
a dihydroxy 3-oxofriedelan from S. reticulata 40