CHAPTER - II

SYNTHESIS OF GUGGULTETROL

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Abstract

To assign the stereochemistry of guggultetrol, optically active diastereoisomers of guggultetrol (1,2,3,4-octadecanetetrol) viz., D-arabino-, D-xylo-, and D-ribo-1,2,3,4-octadecanetetrol were synthesised from two different routes starting from D-glyceraldehyde acetonide and pentoses. The configurational structure of guggultetrol was assigned as "D-xylo-1,2,3,4-octadecanetetrol".

INTRODUCTION

The tetrols isolated from Commiphora mukul are a mixture of 1,2,3,4-octadecanetetrol (50%), 1,2,3,4-nonadecanetetrol (7%) and 1,2,3,4-eicasanetetrol (40%) with minor amounts of other components, possibly lower (C_{16},C_{17}) and higher (C_{21}, C_{22}) homologous tetrols. These tetrols have three asymmetric centres and hence for each tetrol four racemates are possible. It was shown that the various long chain tetrols isolated from C. mukul have the same configuration at the chiral centres.[1]

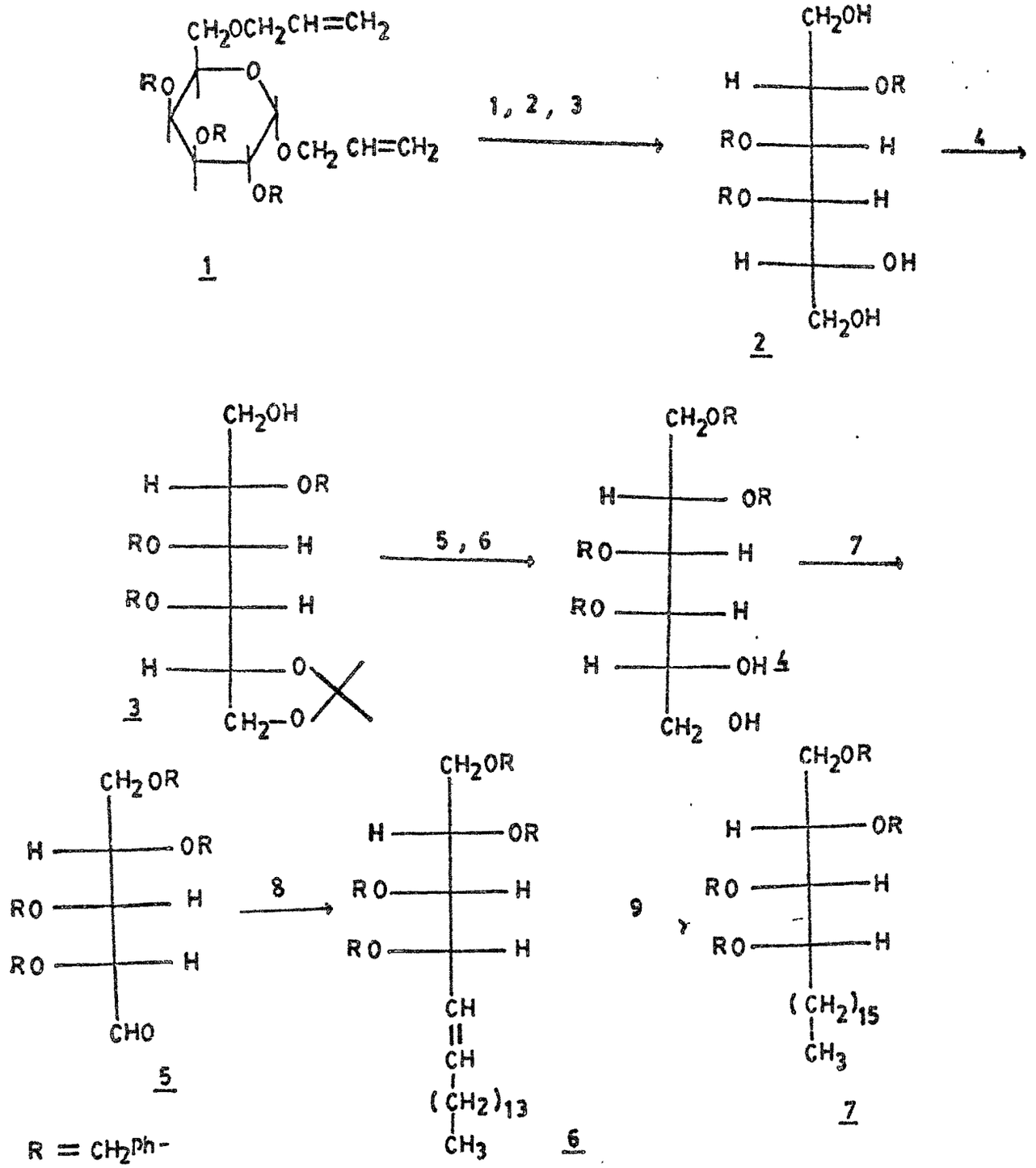
Guggultetrols must have different configuration than that of the synthetic L-arabino-1,2,3,4-eicosanetetrol,[2] which has a quite distinct m.p. (116-119°) than that of the 1,2,3,4-eicosanetetrol (m.p. 85-87°) isolated from C. mukul. (±)-Xylo- and (±)-arabino-1,2,3,4-nonadecanetetrols, and (±)-lyxo-, and (±)-ribo-1,2,3,4-octadecaneterols representing all the four possible stereoisomers of long-chain 1,2,3,4-alkanetetrols have been synthesised and their IR spectra recorded.[3] But it has not been possible to draw any conclusion on the stereochemistry of the guggultetrols by comparing these spectra with that of guggultetrols.[1]

NMR spectra of guggultetrol-diacetonide, guggultetrol-tetraformate, and guggultetrol-tetraacetate do not throw any light on the stereochemistry of the guggultetrols. Hence, to establish the stereochemistry of guggultetrols, optically active diastereo-isomers of 1,2,3,4-octadecane-tetrol, the major component of the tetrol mixture, were synthesised.

Previous Synthesis of Long Chain Tetrols

There are only a few synthetic approaches currently available for the synthesis of 1,2,3,4-long chain tetrols.

The synthetic scheme (Fig. 1) of R. Gigg and C.D. Warren[2] utilizes optically active allyl 6-O-allyl-2,3,4-tribenzyl-α-D-galactopyranoside (1) as a starting material for the synthesis of optically pure L-arabino-1,2,3,4-eicosanetetrol. Crystalline 2,3,4-tri-O-benzyl-D-galactose was prepared from 1 by isomerization of the allyl groups to prop-1-enyl groups and removal by acid hydrolysis, Reduction by sodium borohydride gave the crystalline 2,3,4-tribenzyl-D-galactitol (2), which was converted into crystalline isopropylidene derivative (3). Benzylation of compound (3) and subsequent acid hydrolysis gave 1,2,3,4-tetra-O-benzyl-D-galactitol (4) which on oxidation with periodic acid gave 2,3,4,5-tetra-O-benzyl aldehydo-L-lyxose (5). A Wittig reaction between the aldehyde (5) and the

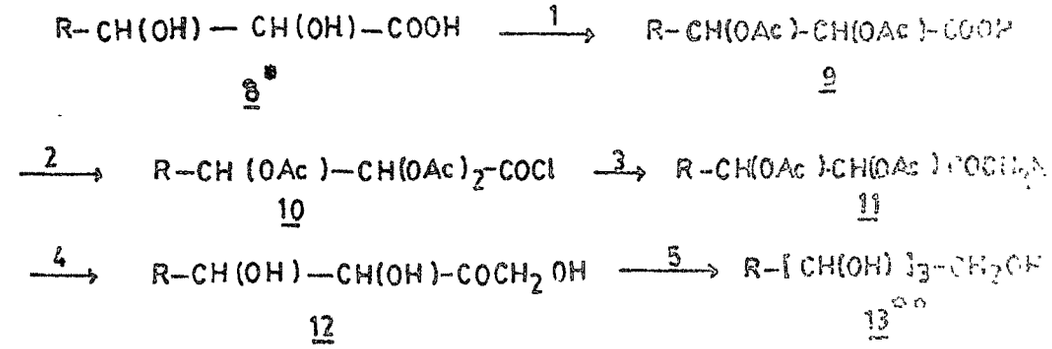


Reagents: - 1. K-t-butoxide/DMSO, 2. $N.H_2SO_4$/acetone, 3. $NaBH_4$/MeOH, 4. P.Ts/acetone, 5. $PhCH_2Cl$/NaOH, 6. $N.H_2SO_4$/MeOH, 7. HIO_4/MeOH, 8. $CH_3(CH_2)_{14}$-Pph_3Br/phLi/ether, 9. 10% Pd/C/AcOH.

Fig. 1

phosphorane prepared from n-pentadecyltriphenylbromide gave the olefin (6), which was reduced catalytically to L-arabino-1,2,3,4-tetrahydroxy eicosane (7).

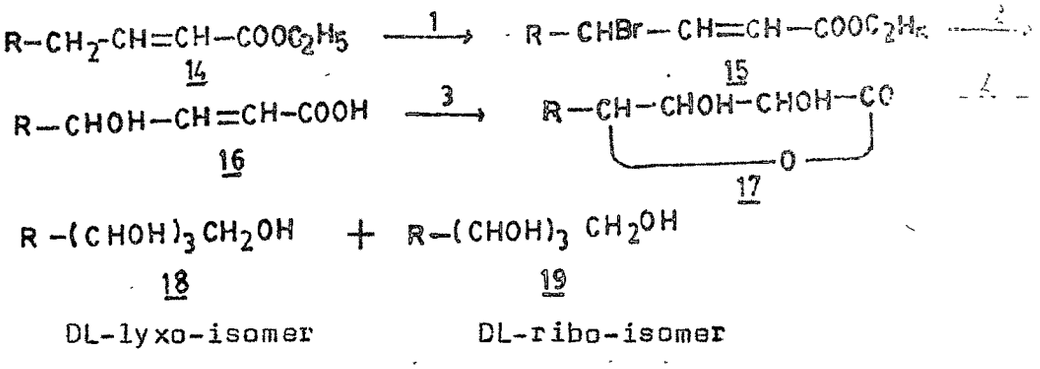
B. Palameta and N. Zambeli[3] have synthesised the four possible long-chain DL-1,2,3,4-alkanetetrols in connection with the synthesis of phytosphingosine. The synthetic scheme of these syntheses are outlined in Fig. 2. DL-xylo-, and DL-arabino-1,2,3,4-nonadecanetetrols were synthesised from 2,3-dihydroxyoctadecanoic acid (8). threo-2,3-Dihydroxy-octadecanoic acid (8a) was acetylated and the diacetate (9a) obtained was converted to the acid-chloride (10a), which on treatment with diazomethane gave diazoketone (11a). This was converted into (12a) by treating with H_2SO_4 in dioxane. LAH reduction of 12a gave the required DL-xylo-1,2,3,4-nona-decanetetrol. The configurational relationships between the hydroxyl substituents on carbon atoms C-3 and C-4 of the products remained unchanged with respect to the original 2,3-dihydroxy acid, and it was shown that the hydroxy substituent on the newly formed assymmetric centre had the threo-configuration. DL-Arabino-1,2,3,4-nonadecanetetrol was synthesised in similar lines starting from erythro-2,3-dihydroxy octadecanoic acid (8b). DL-Ribo-?, and DL-lyxo-1,2,3,4-octadecanetetrols were synthesised starting from 4-hydroxy-trans-2-octadecenoic acid (16). It was obtained from allylic bromination of 14 and subsequent hydrolysis of



*8a = threo-2,3,-Dihydroxyoctadecanoic acid, **13a = DL-xylo-isomer.

8b = erythro-2,3-Dihydroxyoctadecanoic acid, 13b = DL-arabino-isomer

Reagents: - 1. Ac_2O/Pyridine, 2. $SOCl_2$, 3. CH_2N_2/ether,
4. 10% aq. H_2SO_4/dioxane, 5. LAH.



Reagents: - 1. NBS/CCl_4, 2. KOH/EtOH/H_2O
3. AcOH/H_2SO_4/90% H_2O_2, 4. LAH.

Fig. 2

the bromoester (15). Peracid hydroxylation of 16 afforded a mixture of two isomeric lactones (17) from which the tetrols 18 and 19 were obtained by LAH reduction. The configuration of these tetrols was assigned as DL-lyxo-(18) and DL-ribo-(19), based on their IR spectra and melting point.

PRESENT WORK

Carbohydrate intermediates were used as starting materials for the synthesis of optically active diastereoisomers of 1,2,3,4-octadecanetetrol. Carbohydrates have an array of hydroxyl groups and an aldehyde functionality, which was exploited for the introduction of long chain by Wittig reaction followed by hydrogenation.

D-xylo-1,2,3,4-octadecanetetrol, D-arabino-1,2,3,4-octadecanetetrol and D-ribo-1,2,3,4-octadecanetetrol were synthesised by two different routes starting from D-glyceraldehyde and D-pentoses.

1. Synthesis of D-xylo-1,2,3,4-octadecanetetrol, D-arabino-1,2,3,4-octadecanetetrol and D-ribo-1,2,3,4-octadecanetetrol, from D-glyceraldehyde acetonide

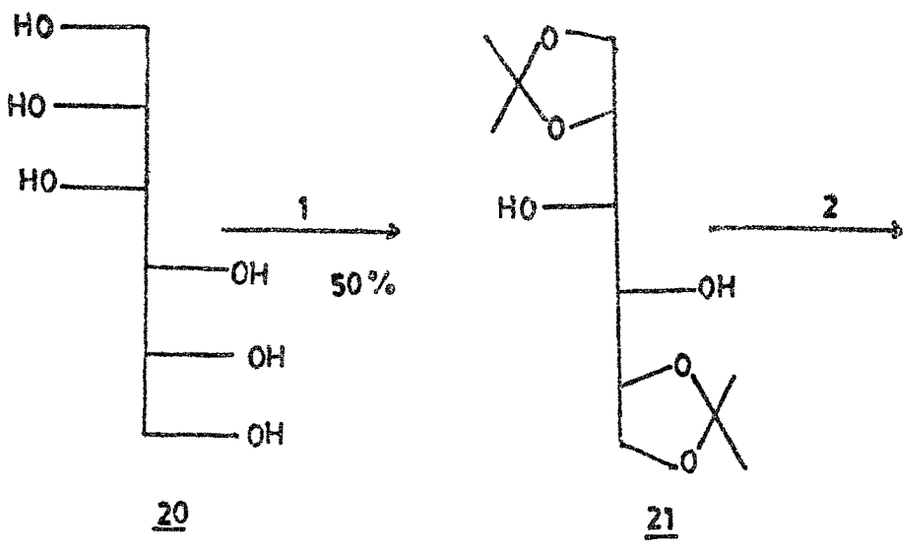
D-glyceraldehydeacetonide has been used very extensively

for the synthesis of biologically active compounds,[4] like prostaglandins[5], amino acids,[6] and an unnatural enantiomer of the antibiotic pyridindolol.[7] Recently, pentitols[8,9], and hexitols[8] have also been synthesised from D-glyceraldehyde acetonide.

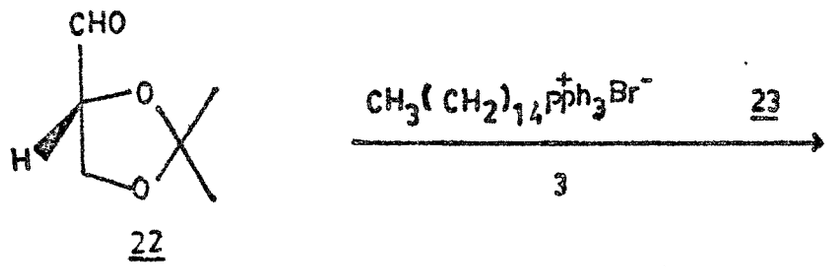
D-glyceraldehyde acetonide seemed to be ideal precursor for the synthesis of optically active diastereoisomers of 1,2,3,4-octadecane tetrol, as it has the right configuration at C-2 carbon atom, and an aldehyde functionality for the introduction of the long chain using stereoselective Wittig reaction[10] leading to a cis-olefin. The resulting cis-olefin can be subjected to stereospecific dihydroxylations to furnish the required tetrols.

D-Glyceraldehyde acetonide (22) was prepared from D-mannitol[11] (Fig. 3). D-Mannitol was converted into the diacetonide-D-mannitol (21) by treatment with dry acetone and anhydrous zinc chloride. The cleavage of the diacetonide-D-mannitol (22) was carried out using lead tetraacetate in dry benzene. The resulting aldehyde was very unstable and hence it was used in the next step without being isolated (from lead tetraacetate cleavage).

The Wittig salt, pentadecyltriphenylphosphoniumbromide(23)



20 21



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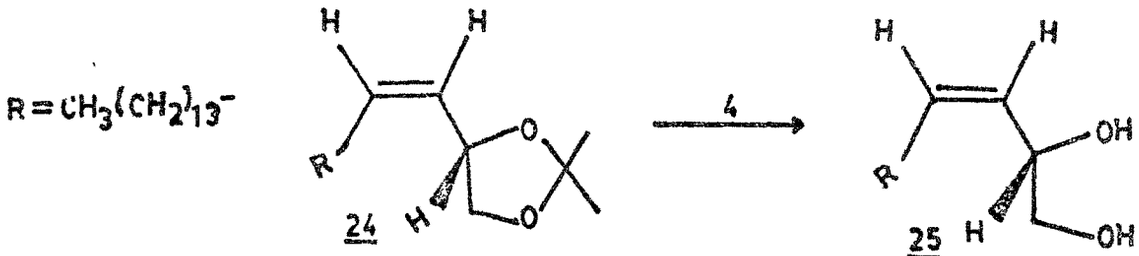


24 25

Reagents: - 1. Acetone/$ZnCl_2$, 2. LTA/C_6H_6,
3. PhLi/Et_2O, 4. 10% aq. $HClO_4$/dioxane.

Fig. 3

was earlier prepared by Jill Cunnigham and Roy Gigg[12] by heating pentadecyl bromide and triphenylphosphine at 140° for 5 hr. However, this reaction furnished a glassy material, instead of a crystalline solid (m.p. 92°), as reported. Attempts to prepare 23 by refluxing the pentadecylbromide and triphenylphosphine in benzene[13] and toluene[13] furnished the product of similar nature. However, acetonitrile was found to be suitable solvent for this reaction, when pentadecylbromide and triphenylphosphine were refluxed in dry acetonitrile and the product on treatment with dry ether furnished the crystalline solid (m.p. 90°) of pentadecyltriphenyl phosphoniumbromide (23). Pentadecylbromide was prepared from palmitic acid by Hunsdiecker reaction.[14]

It is known that, Wittig reaction of the reactive phosphoranes (alkylidene phosphoranes) with carbonyl compounds in non-polar solvents like benzene, ether etc. in the absence of salts, leads to the formation of olefin mixture, in which cis-isomer predominates.[10,15] We therefore tried the Wittig reaction of the D-glyceraldehyde acetonide (22) with pentadecyltriphenylphosphorane in benzene/ether solvent mixture. Pentadecyltriphenylphospharane soln was obtained by treating the Wittig salt (23) with phenyllithium in ether and filtering the salts formed during the generation of red coloured phesphorane. To this soln of phospharane, was added a soln of 22. After refluxing for 6 hr and the

usual work-up gave a single olefin (24) which was assigned cis-geometry from its IR spectrum. The olefin exhibited no absorption at about 965 cm^{-1}, a characteristic of trans-isomer[16,17]. The cis-olefin (24) exhibited the spectral characteristics expected of 24. IR (Fig. 13): (neat) C=C 1660 cm^{-1}, gemdimethyl, 1375 and 1385 cm^{-1}. PMR (Fig. 14): C=C-H, 2H, m, 5.4 ppm. Mass (Fig. 15): m/e 324 (M^+, 8.16%).

The cis-olefin acetonide (24) was then hydrolysed with 10% aq. perchloric acid in dioxane to cis-olefindiol, which was repeatedly crystallized to constant melting point (58-59°). This olefinic diol (25) was reprotected to the cis-olefin acetonide, which exhibited the same spectral characteristics as the total product described earlier. This indicates that the crude Wittig product was essentially only a cis-olefin acetonide. However, purified 24 was used in the dihydroxylation reactions.

(a) Synthesis of D-xylo-1,2,3,4-octadecanetetrol and D-arabino-1,2,3,4-octadecanetetrol: The trans-dihydroxylation of the cis-olefin acetonide was expected to give D-xylo-, and/or D-arabino-isomers (Fig. 4).

For trans-dihydroxylation of olefins, performic acid

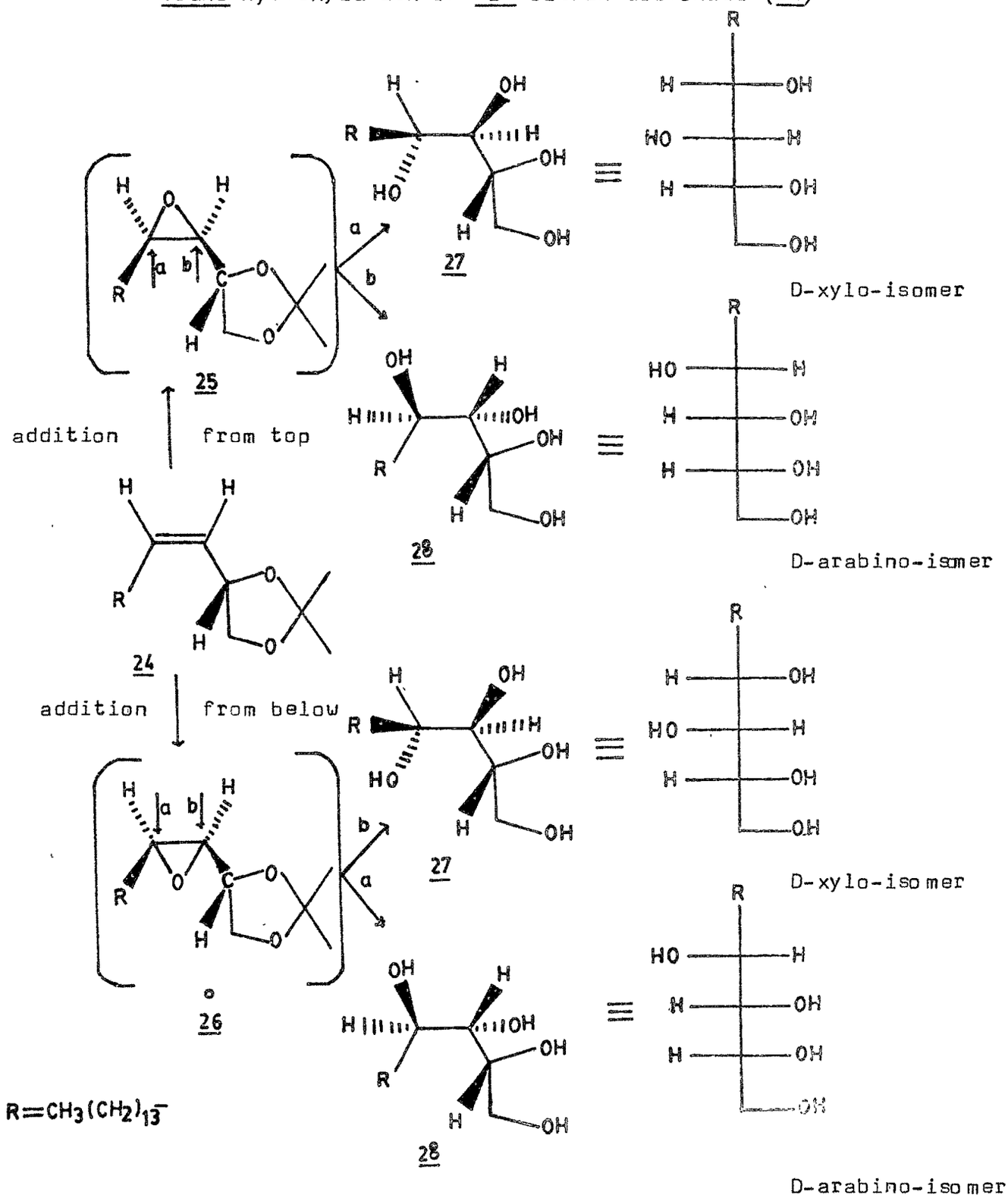
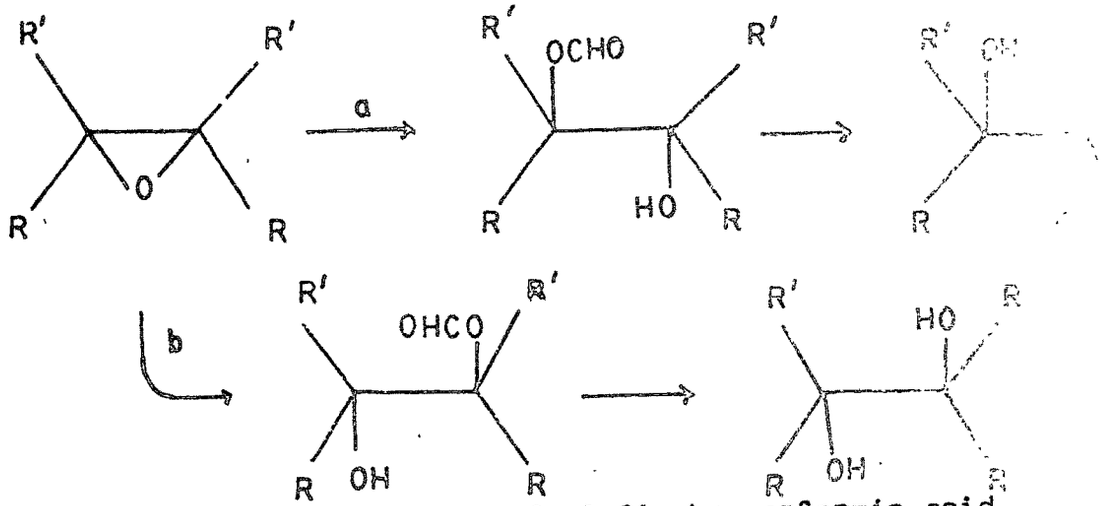

trans-Hydroxylation of cis-olefin acetonide (24)
addition from top
addition from below
R=CH3(CH2)13-
25
26
27
28
24
D-xylo-isomer
D-arabino-isomer
D-xylo-isomer
D-arabino-isomer

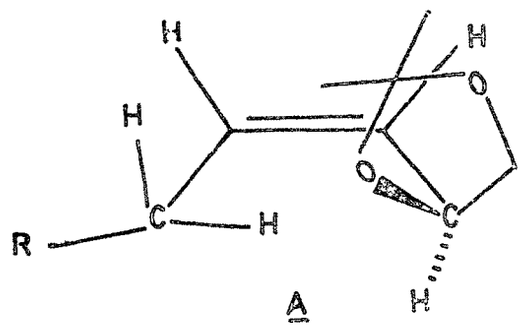
Fig. 4

is the frequently used reagent.[18,19] Performic acid when treated with an olefin, forms an epoxide which is then cleaved by formic acid with opening of the oxirane-ring in one or both possible directions to give a monoformate or monoformate mixtures (Fig. 5).[18] In usual practice, the material is precipitated with water and hydrolysed with alkali to give trans-diol mixture.

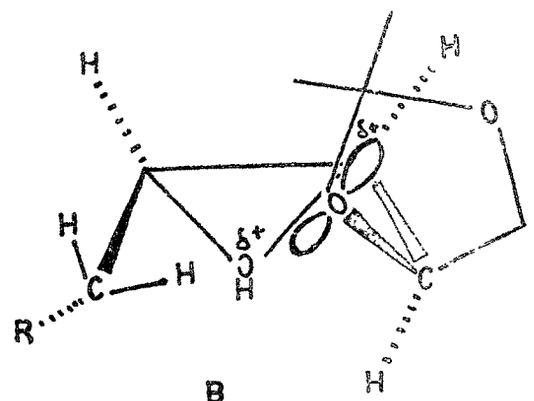
In case of cis-olefin acetonide (24), a study of molecular models (Dreiding) revealed that the conformation A (Fig. 5) is oreferred since it is sterically least strained. In conformation A of 24, the top surface (the face bearing O-alkyl group) is shielded by one methyl group of the isopropylidene moiety. Therefore the initial attack of the performic acid on double bond of the 24 would be expected to occur from below surface (opposite to the face bearing O-alkyl group), which is sterically less hindered. Considering this conformational preference of 24, we expected a stereospecific epoxidation leading to 26 (Fig. 4). The acid catalysed cleavage of the resulting epoxide (26) might occur from either directions a or b (26, Fig. 4). On the basis of a bimolecular reaction pathway and consideration of the inductive substituent effects which are believed to govern the regiochemistry of the opening, direction a is preferred.[20] However, there are reports[21,22], where



trans-Dihydroxylation of olefin by performic acid.



A



B

Most preferred conformation of 24 (from molecular model study).

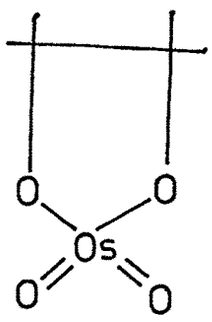
Fig. 5

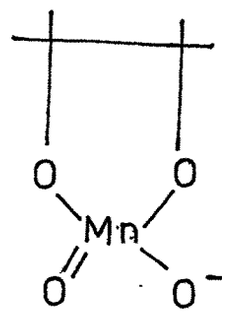
direction b was preferred. In case of 26, direction b was expected to be preferred, because the incipient carbonium ion in the transition state at carbon atom C-3 will be stabilized through lone pair interaction on oxygen atom of isopropylidene acetal group(B, Fig. 5), whereas there is no such stability conferred to the incipient carbonium ion arising from other cleavage (a, Fig. 4). As a consequence, a regioselective opening of the epoxide (26) was expected to give D-xylo-1,2,3,4-octadecanetetrol as a major product.

In practice, when 24 was treated with performic acid, two products were formed; the major one D-xylo-1,2,3,4-octadecanetetrol [30%, m.p. 83-84°, IR (Fig. 21): (KBr-Pellet) OH 3420 cm^{-1}, 3320 cm^{-1}. PMR (Fig. 22): (DMSO-D_6): O-CH, 3H, 3 bm, 3.75 ppm) 3.94 ppm and 4.2 ppm. Mass (Fig. 23): m/e 319 (M^++1, 1%)] and the minor D-arabino-1,2,3,4-octadecanetetrol [15%, m.p. 136-137°, IR (Fig. 19): (KBr-pellet): OH 3350, 3240 cm^{-1}. Mass (Fig. 20): m/e 269 (M^+-49; 2%)]. The stereochemistry of these products was confirmed by correlation with the authentic samples synthesised from pentose route (Figs. 9 and 10), in the usual manner (m.p., m.m.p., IR, optical rotation). These results are in good agreement with our theoritical predictions.

(b) Synthesis of D-ribo-1,2,3,4-octadecanetetrol: cis-Dihydroxylation of 24 was expected to yield D-lyxo-, and/or D-ribo-1,2,3,4-octadecanetetrols (Fig. 6).

For cis-dihydroxylation of olefins osmium tetroxide and alkaline potassium permanganate are the most commonly used reagents.[23] The mechanism of the reaction involves the initial formation of a permanganate and osmate esters. The osmate ester is converted to the glycol, preferably by a reductive cleavage of Os-O-bond, while the glycol is obtained





from permanganate ester by hydrolysis.[23]

Metal chlorates like potassium, sodium, barium etc. are used along with catalytic amount of osmium tetroxide for the cis-dihydroxylation of the olefins.[24] These oxidations presumably occur through the formation of an osmium (VI) ester complex, which is hydrolysed by chlorate

<u>cis</u>-Dihydroxylation of <u>cis</u>-olefin acetonide (<u>24</u>)

($OsO_4/NaClO_3$)

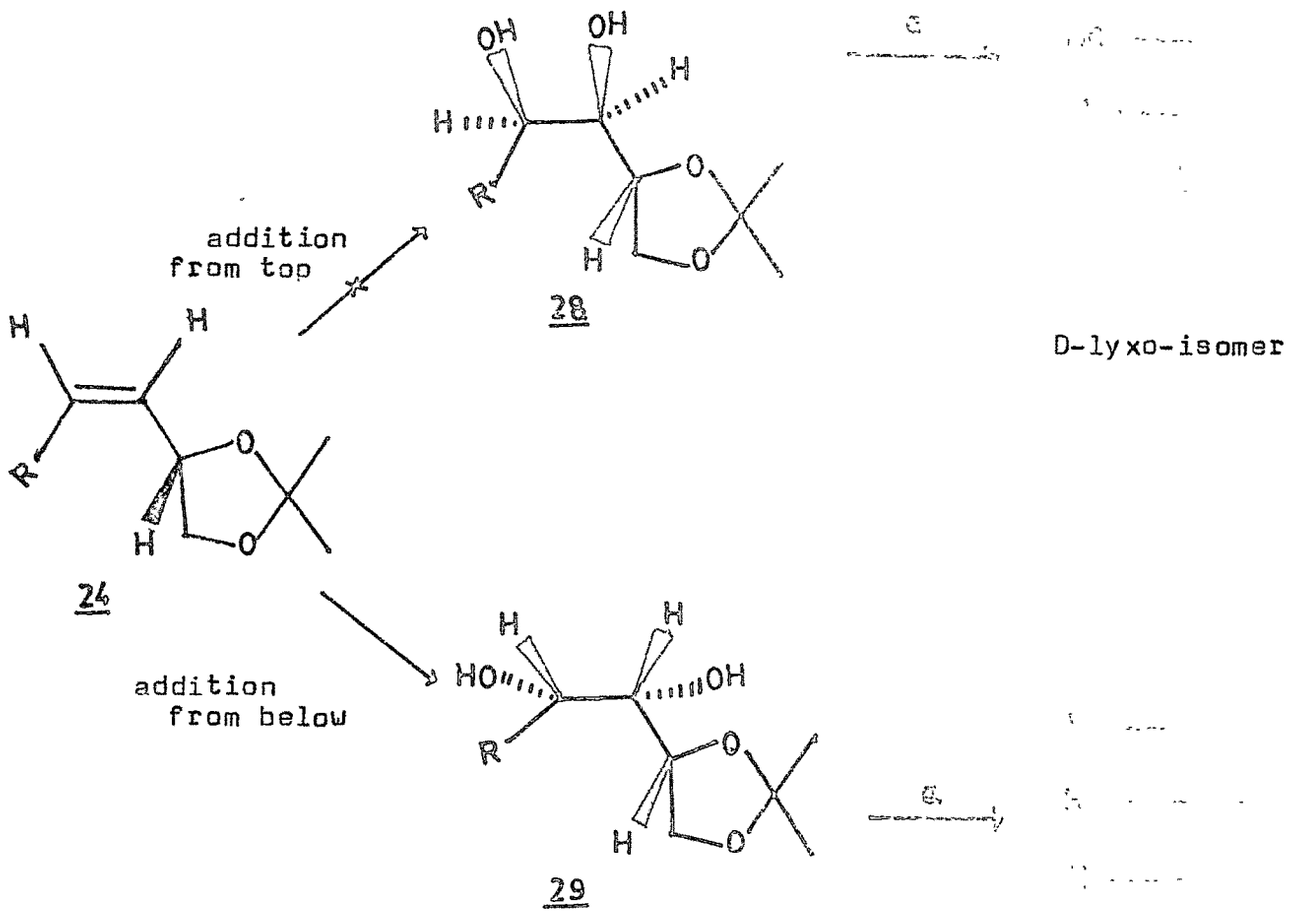


Fig. 6

ion to regenerate osmium tetroxide.[24]

In the case of cis-olefin-acetonide (24, conformation A, Fig. 5), the osmium tetroxide would approach the double bond from the below surface (ooposite to the face bearing O-alkyl group), as it is less hindered. And hence we expected stereospecific cis-dihydroxylation resulting in the formation of D-ribo-isomer.

Osmylation of the 24 was carried out using OsO_4 and sodium chlorate in aq. tetrahydrofuran. Reaction was complete in 3 hr. The crude product was hydrolysed using aq. $HClO_4$ in dioxane. From the resulting crude product, a crystalline solid was isolated in 15% yield by chromatography, which was identified as D-ribo-1,2,3,4-octadecanetetrol by comparing with the authentic sample synthesised by pentose route (Fig. 8). This result is in good agreement with our theoretical prediction as well as with the empirical formulation of the stereochemical outcome of osmylation of allylic alcohols and their derivatives proposed by Y. Kishi and co-workers.[9] D-ribo-isomer exhibited the following spectral characteristics. IR(Fig. 25)(KBr-pellet): OH 3420, 3350 cm^{-1}. PMR (Fig. 26) (DMSO-D_6): O-C$\underline{H}_2$, 2H, b, 3.5 ppm, O-C$\underline{H}$, 2H, d, 4.2 ppm; 1H, b, 4.4 opm. Mass (Fig. 27): m/e 284 (M^+-34, 11.9%).

Thus synthesised, D-xylo-, D-arabino-, and D-ribo-1,2,3,4-octadecanetetrols were compared with the guggultetrol in order to assign the stereochemistry of the latter.

D-Arabino-1,2,3,4-octadecanetetrol (m.p. 136-137^{o}) and D-ribo-1,2,3,4-octadecanetetrol (m.p. 116-117^{o}) have quite distinct m.p. and IR spectra from that of the natural product (m.p. 82-83^{o}), and hence the absolute stereochemistry of the natural product is not that of these two isomers. Whereas, D-xylo-1,2,3,4-octadecanetetrol is identical with the natural product (IR, Mass, m.p. m.m.p, optical rotation), and di-O-isopropylidene D-xylo-1,2,3,4-octadecanetetrol which was prepared by treating D-xylo-isomer with dry acetone in presence of anhydrous ferric-chloride, is identical with the di-O-isopropylidene derivative of the natural product. Hence the natural product is

"D-xylo-1,2,3,4-octadecanetetrol".

This clarrifies the stereochemistry of guggultetrol.

The physical constants and spectral data of D-xylo-, D-arabino-, D-ribo-1,2,3,4-octadecanetetrols and guggultetrol are given in the Table 1.

Table 1. Physical and spectral data of guggultetral and 1,2,3,4-octadecanetetrols

Compound	1,2,3,4-octadecanetetrol			
	Guggultetrol	D-xylo-	D-arabino-	D-ribo-
m.p.	82-83°	83-84°	136-137°	116-117°
$[\alpha]_D$ in EtOH	+ 11.4(C.34%	+10(C.11%)	+50(C.05%)	-8.86(C.44%)
IR	(nujol) 3400, 3200,2920,2850, 1470,1142,1070, 850 cm^{-1}	(KBr-pellet) 3420,3320, 2920,2850, 1465,1138, 1070,850 cm^{-1}	(KBr-pellet) 3350,3245, 2920,2840, 1460,1406, 1255,1110, 1076 cm^{-1}	(KBr-pellet) 3420,3350, 2920,2850, 1465,1215, 1068,1040, 1020,714 cm^{-1}.
PMR* CH_2,C CH_3 CH_3	2s, 1.25 ppm 1.30 ppm	2s, 1.25ppm 1.30ppm	s, 1.30ppm	s, 1.30 ppm
O-CH_2	1H,dd,3.5ppm (J_{gem}=8Hz, J_{vic}=2Hz) 1H,3.9 ppm	1H, dd 3.50 ppm (J_{gem}=8Hz, J_{vic}=2Hz) 1H, 3.9 ppm	bm,3.38ppm	bm,3.55ppm
O-CH	bm,3.9 ppm	bm, 3.9 ppm	bm, 3.9ppm	bm, 3.88ppm
Mass m/e	319(M^++1,0.3%) 97(7%),85(12%) 74(100%),73 (9%),69(14%), 61(10%), 57 (20%), 56(21%).	319(M^++1,1%) 97(10%),85(8%) 74(100%), 73 (12%), 69 (34%),61(20%)	269(M^+-49,2%) 258(2%),74 (100%),69 (41.6%),67 (21.8%).	284(M^+-34, 11.9%) 264(19.9%), 257(10.6%), 256(58.6%), 213(13.3%), 55(100%).

* PMR values given are for the di-O-isopropylidene derivatives of tetrols.

2. Synthesis of D-ribo-1,2,3,4-octadecanetetrol, D-xylo-1,2,3,4-octadecanetetrol and D-arabino-1,2,3,4-octadecanetetrol from respective pentoses

For the synthesis of 1,2,3,4-octadecanetetrols of known stereochemistry, pentoses are the right starting materials, as they have four hydroxyl groups, which will become the hydrophilic asymmetric part of the tetrols, and an aldehyde functionality to introduce the long-side chain by Wittig reaction followed by hydrogenation of the resulting olefin. In this case, the absolute stereochemistry of the final product is unambiguous as it is prefabricated by choosing the right pentose.

The course of the reaction of phosphoranes with sugars is unambiguous only when protected aldehydo- or ketosugars are used.[25] Although partially protected and even unprotected aldoses were shown amenable to the reaction with various resonance stabilized phosphoranes. The latter reactions however, are extremely complicated[25]. When D-ribose was subjected to Wittig reaction with tridecyltriphenylphosphorane in DMF, the reaction failed to yield the required tetrol. Hence we planned to use protected aldehydo-pentoses in the synthesis of various 1,2,3,4-octadecanetetrols.

A typical sugar e.g., glucose exists in soln as an

equilibrium mixture of the acyclic (32) and cyclic (furanose, 35; and pyranose, 36) (Fig. 7) forms. The aldehydo form (32) can be trapped as dithioacetal (37). This dithioacetal after protecting the hydroxyl groups (all, or the ones which are participating in the ring formation) with suitable protecting groups, can be transformed to free aldehydo-sugar.

In the present case the hydroxyl groups of the pentose-diethyldithioacetals were protected as O-isopropylidene groups,[26,27] as it is very stable in the basic conditions of the Wittig reactions. Thus, D-ribo-1,2,3,4-octadecanetetrol, D-xylo-1,2,3,4-octadecanetetrol, and D-arabino-1,2,3,4-octadecanetetrol were synthesised from D-ribose, D-xylose, and D-arabinose respectively.

(a) Synthesis of D-ribo-1,2,3,4-octadecanetetrol from D-ribose. D-ribo-1,2,3,4-octodecanetetrol was synthesized from D-ribose as outlined in Fig. 8. D-ribose diethyl-dithioacetal (38) was prepared in 80% yield by treating D-ribose with ethanethiol in aq. hydrochloric acid.[28] 2,3,4,5- and 2,4,3,5-di-O-Isopropylidene-D-ribose diethyl-dithioacetals (39) were earlier[29] prepared by treating 38 with dry acetone and anhydrous copper sulfate for 36 hr, in 80% yield. However this reaction furnished 39 in

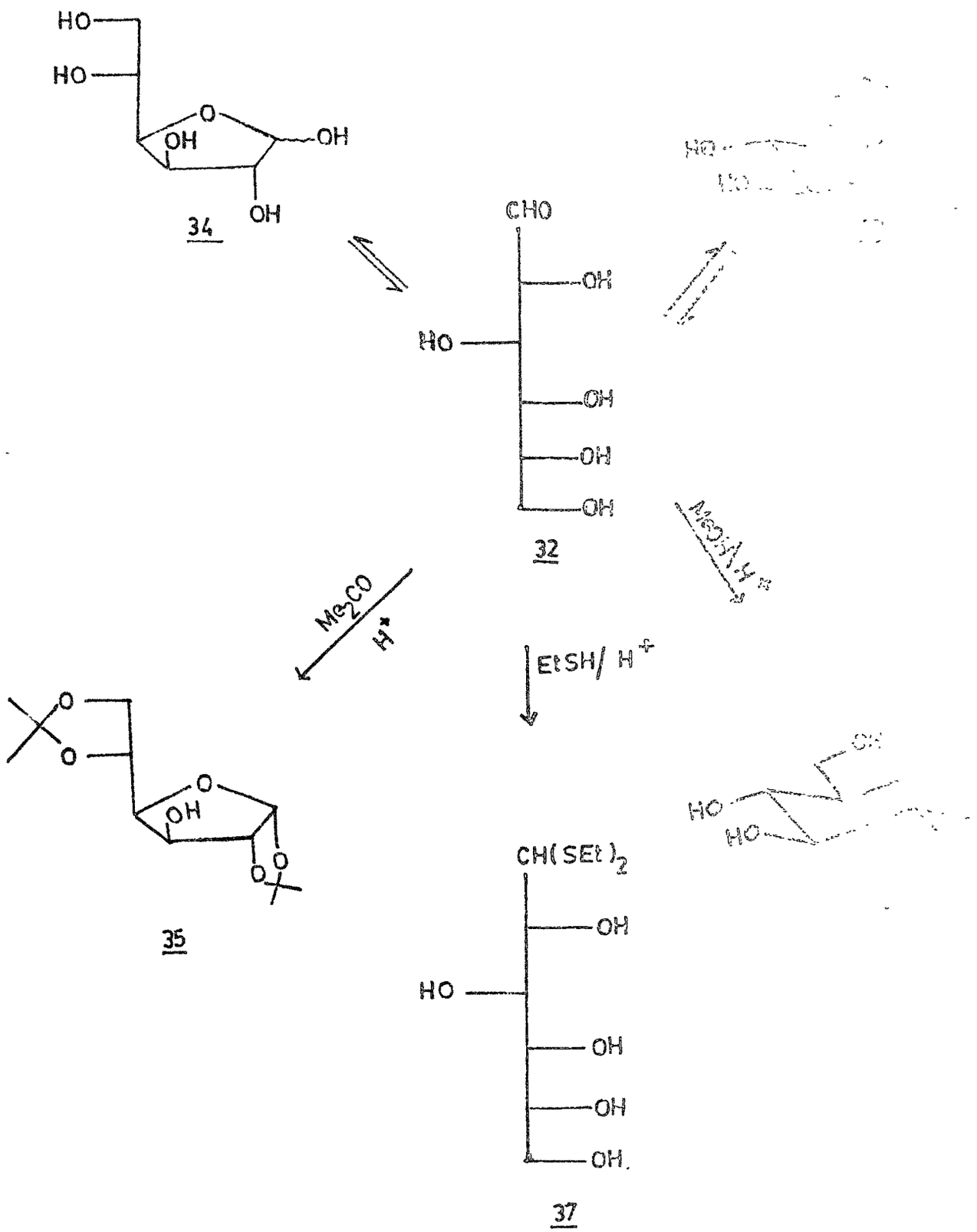
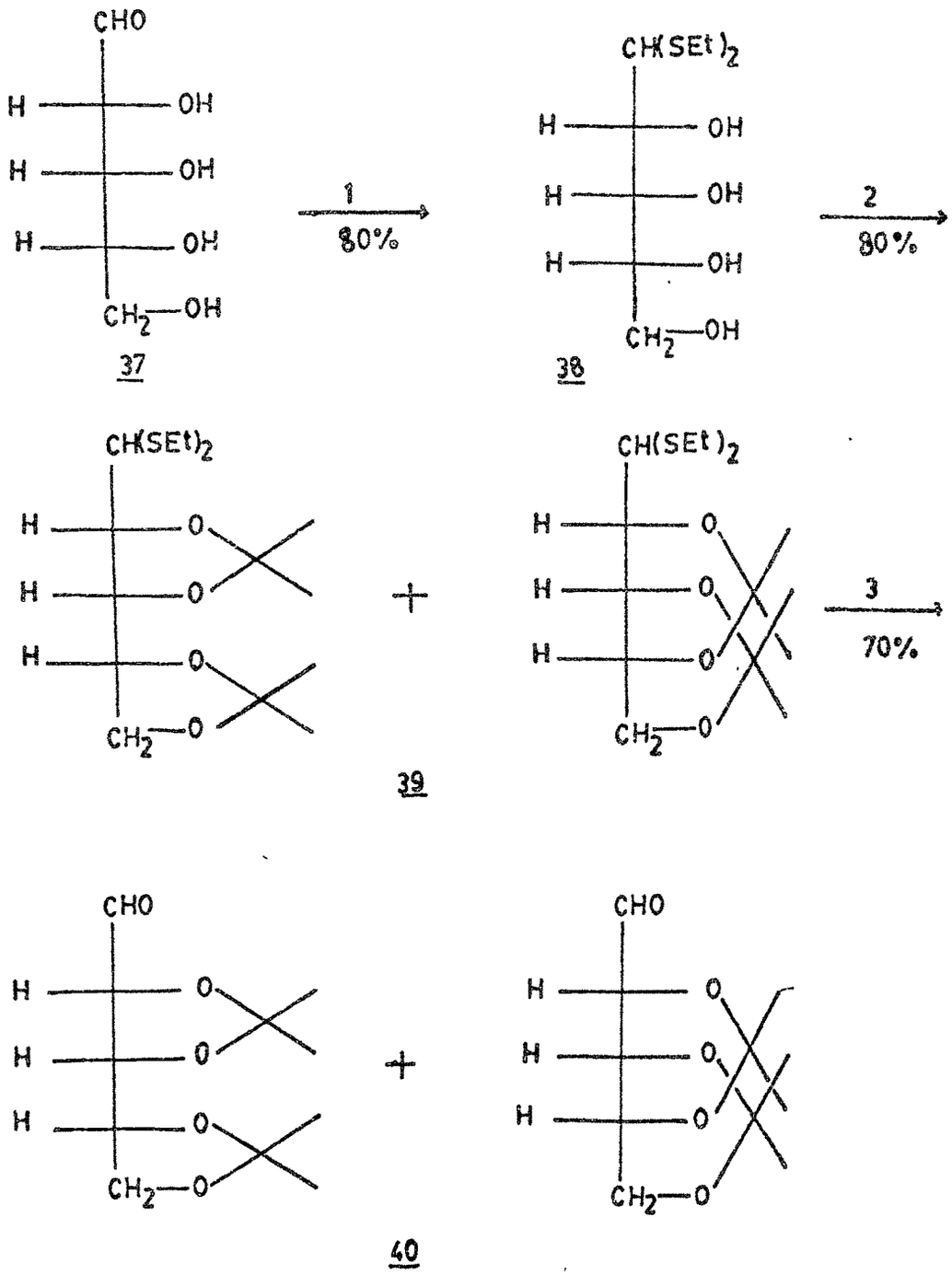
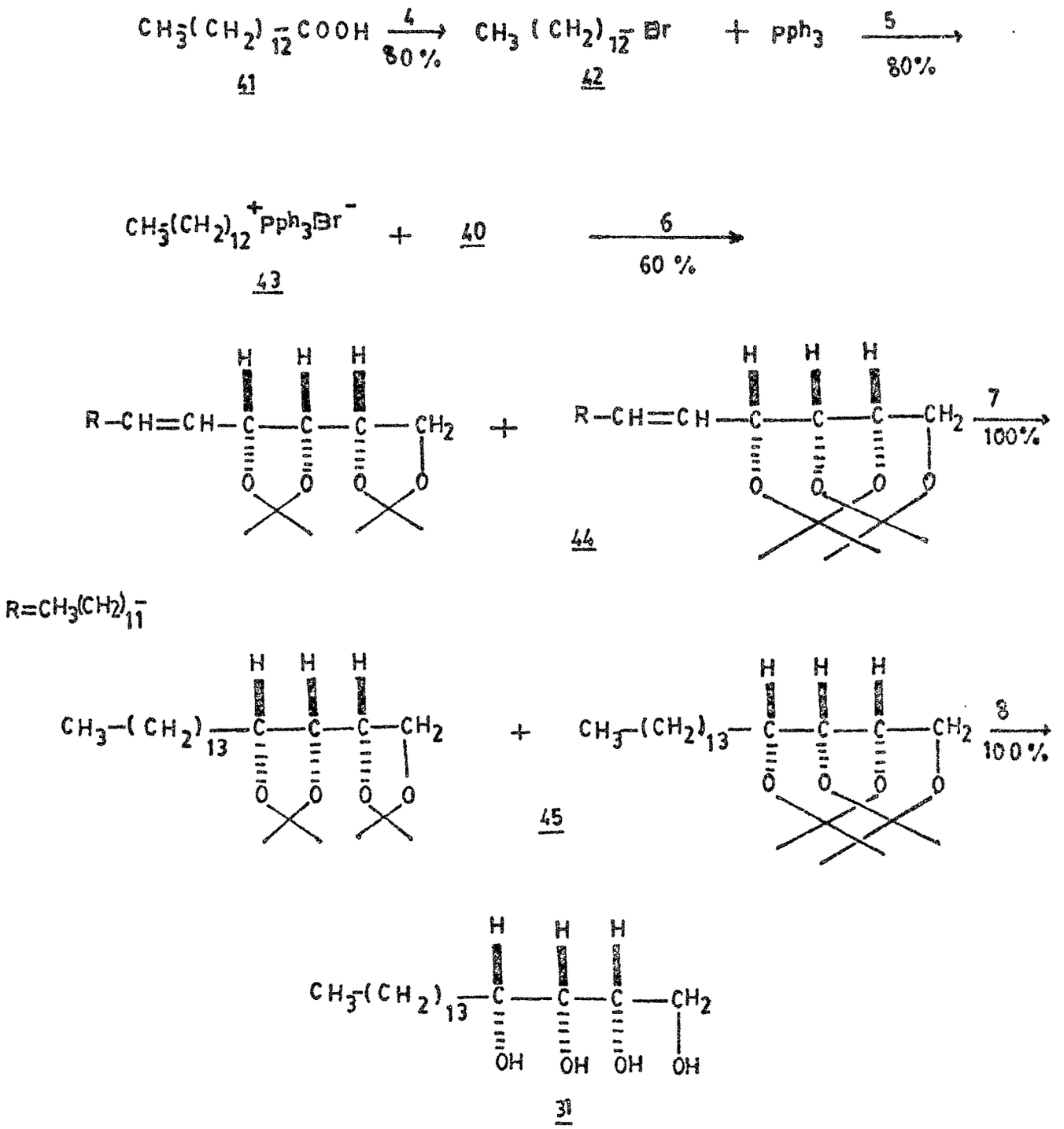

HO
HO
O
OH
OH
OH
34
CHO
OH
HO
OH
OH
OH
32
Me2CO
H+
EtSH/ H+
O
O
O
OH
O
O
35
CH(SEt)2
OH
HO
OH
OH
OH
37

Fig 7



Reagents: - 1. EtSH/HCl, 2. $Me_2CO/FeCl_3$, 3. $HgCl_2/CdCO_3$/aq. MeCN.

Fig. 8 (contd.)



Reagents:- 4. Br_2, HgO/CCl_4, 5. MeCN, reflux,
6. PhLi/THF, 7. 10% pd/C, EtOH, 8. 10% $HClO_4$/ dioxane.

Fig. 8

70% yield only. In this reaction anhydrous copper-sulfate acts as dehydrating reagent, taking up water which is formed in the reaction.[30] Because of long reaction time as well as only moderate yield using this reagent, we tried molecular sieves (5A) and anhydrous ferric chloride as catalysts, instead of anhydrous copper sulfate in this reaction. The reaction was sluggish in case of molecular sieves and even after 48 hr, there was no complete conversion. Hence, this reagent was not pursued further.

Although anhydrous ferric chloride is known to do isopropylidenation of sugars,[31] presumably no such reaction has been tried with sugar dithioacetals. It was a pleasure to discover that, when diethyl dithioacetal (38) was treated with dry acetone in presence of anhydrous ferric-chloride, isopropylidenation was complete within an hour, to furnish fully protected dithioacetal (80% yield) and only a small amount of partially protected dithioacetal was formed. The ratio of 2,3,4,5-, and 2,4,3,5-di-O-isopropylidene-D-ribose diethyldithioacetal (39) was almost same as earlier reported (3:2).[29]

Regeneration of the aldehyde functionality was achieved by treating 39 with mercuric chloride and cadmium carbonate in aq. acetonitrile. Acetonitrile was found to be a better

solvent as compared to acetone, which was used earlier for this purpose.[32] In case of acetone some by-products were forming, which were completely eliminated by using acetonitrile.

For the next step, the Wittig salt, tridecyltriphenylphosphonium bromide (43) was prepared in a similar way as described for pentadecyltriphenylphosphonium bromide (23). Tridecylbromide itself was readily obtained by the Hunsdicker reaction of the myristic acid (41). The Wittig reaction of the aldehyde (40) with 43 in presence of phenyllithium afforded olefins, which were isolated in 60% yield by chromatography. The structure of olefins (44) was fully borne out by their spectral data. IR (Fig. 27) (Neat): C=C, 1658 cm^{-1}, gemdimethyl 1380 and 1370 cm^{-1}. PMR (Fig. 28) (CCl_4): C=C-H, 2H, bm, 5.45 ppm. Mass (Fig. 29): m/e 396 (M^+, 1.08%).

The olefin mixture (44) was hydrogenated in presence of 10% palladium on charcoal in absolute alcohol. The resulting tetrol-di-O-isopropylidene exhibited following spectral characteristics.
IR (Fig. 30) (CCl_4): gemdimethyl 1385 cm^{-1} and 1375 cm^{-1}.
PMR (Fig. 31): O-CH, 3H, bm, 3.9 ppm.
Mass (Fig. 32): m/e 398 (M^+, 1.3%). 45 was hydrolysed with 10% aq. $HClO_4$ in dioxane, to furnish D-ribo-1,2,3,4-octadecanetetrol, which was crystallized from absolute

alcohol (m.p. 116-117°).

(b) D-xylo-1,2,3,4-octadecanetetrol from D-xylose. D-xylo-1,2,3,4-octadecanetetrol was synthesised from D-xylose (Fig. 9) in similar lines as described for D-ribo-1,2,3,4-octadecanetetrol. D-xylosediethyldithioacetal (47) was prepared from D-xylose by treating it with ethanethiol in aq. hydrochloric acid.[19] 2,3,4,5-Di-O-isopropylidene-D-xylosediethyldithioacetal (48) was prepared in 85% yield using anhy. ferric chloride as compared to reported 73% yield, using anhydrous cooper sulfate.[19] Di-O-isopropylidene (48) was converted into the aldehyde (49), which was then subjected to Wittig reaction with the Wittig salt (43). The resulting olefin was isolated in 60% yield by chromatography. The structure of the olefin (50) was fully borne out by its spectral data.

IR (Fig. 33) (CCl_4): C=C 1625 cm^{-1}.

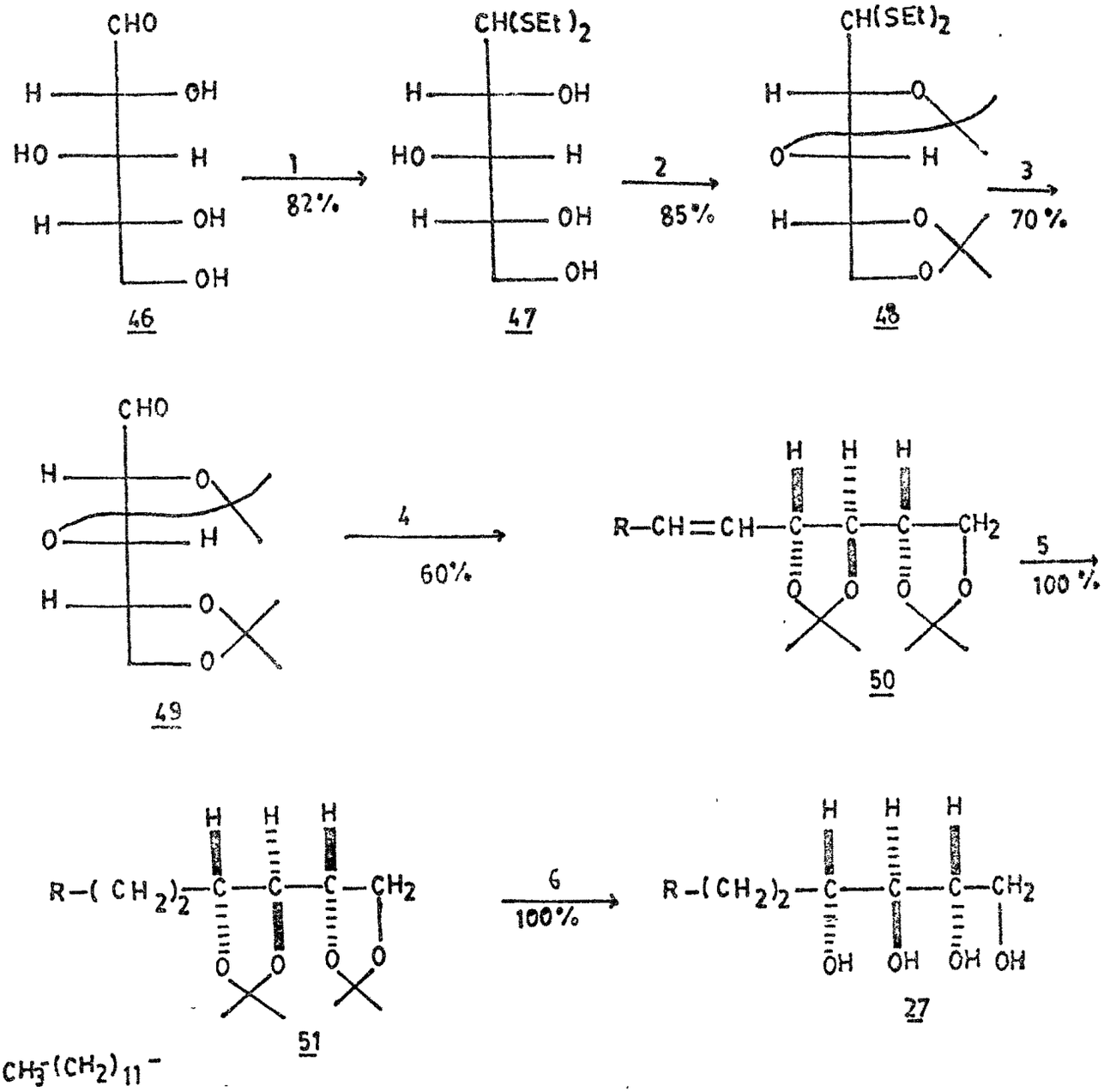
PMR (Fig. 34) (CCl_4): C=C-H 2H, bm, 5.5 ppm.

Mass (Fig. 35): m/e 396 (M^+, 5.7%).

On hydrogenation over 10% palladium/charcoal, the olefin (50) furnished the di-O-isopropylidene-D-xylo-1,2,3,4-octadecanetetrol (51) which displayed the following spectral characteristics.

IR (Fig. 36) (CCl_4): gemdimethyl 1385 cm^{-1} and 1375 cm^{-1}.

PMR (Fig. 37): O-CH,3H, bm, 3.9 ppm; O-CH_2,2H, 2b, 3.58 ppm and 349 ppm. Mass (Fig. 38): m/e 398 (M^+, 4.63%).



Reagents : 1. EtSH/HCl, 2. $Me_2CO/FeCl_3$,
3. $HgCl_2$, $CDCO_3$/aq. MeCN, 4. $CH_3(CH_2)_{13}$-Pph_3Br, phLi/THF, 5. 10% pd/C, EtOH, 6. 10%aq.$HClO_4$/ dioxane.

Fig. 9

Di-O-isopropylidene (51) on treatment with 10% aq. $HClO_4$ in dioxane furnished D-xylo-1,2,3,4-octadecanetetrol (27), which was crystallized from absolute alcohol (m.p. 83-84°).

(c) D-arabino-1,2,3,4-octadecanetetrol from D-arabinose.

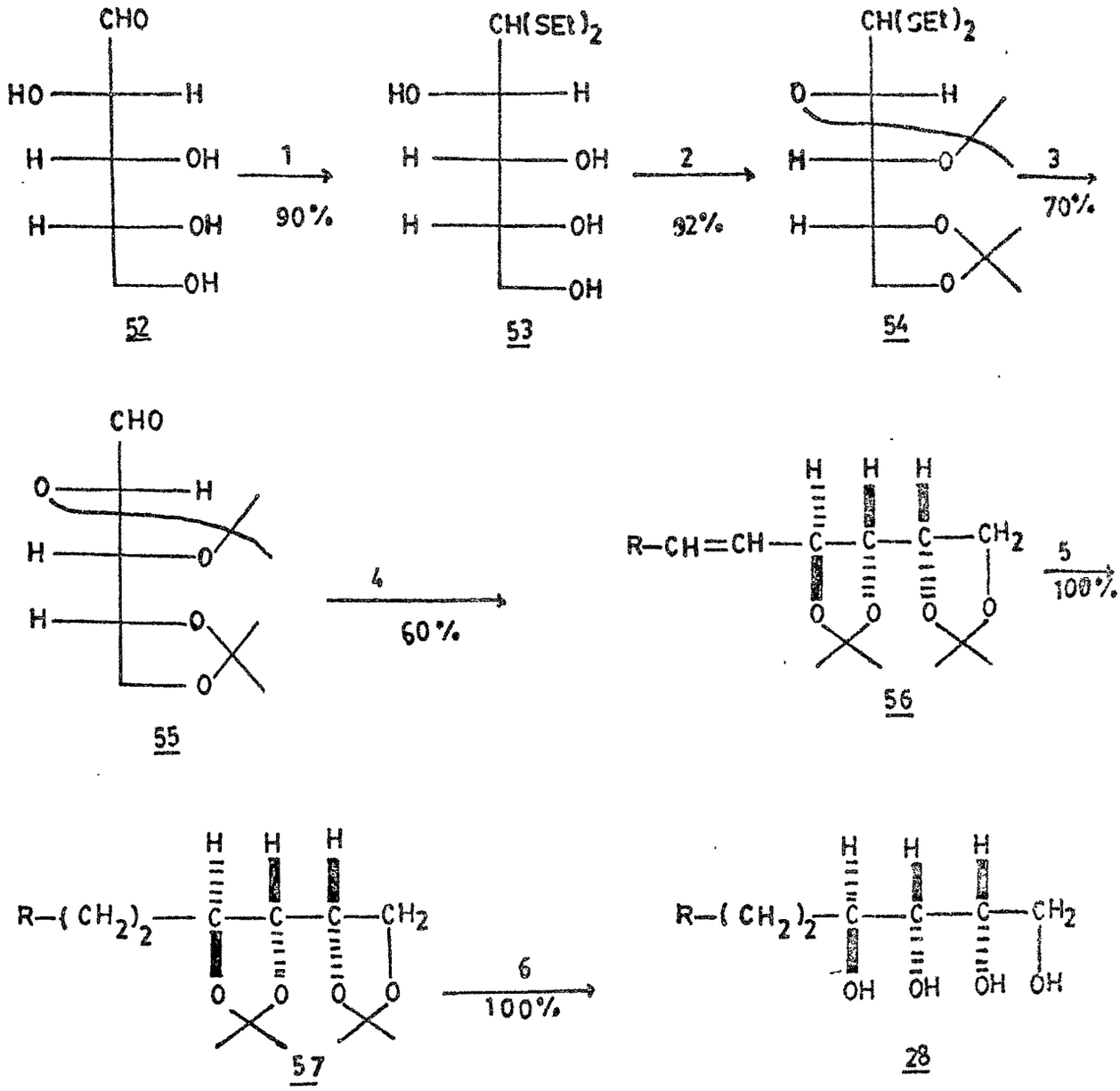
D-arabino-1,2,3,4-octadecanetetrol (28) was synthesized following similar route (Fig. 10) as described for D-ribo-, and D-xylo-isomers.

D-Arabinosediethyldithioacetal (53) was prepared in 90% yield and was converted to di-O-isopropylidene derivative in 92% yield by ferric chloride catalysed isopropylidenation as compared to 75% yield by conc. sulfuric acid catalysed isopropylidenation.[33] In all the three isopropylidenation reactions of thioacetals (38, 47 and 53) anhy. ferric chloride was found to be far superior reagent than the ones earlier used for this reaction. The aldehyde (53) was obtained from 52, in 70% yield underwent Wittig reaction smoothly, furnishing the olefin (56) in 60% yield, which exhibited the spectral characteristics expected of (56).

IR (Fig. 39) (CCl_4): C=C 1630 cm^{-1}.

PMR (Fig. 40): C=C-H, 2H, m, 5.92 ppm.

Hydrogenation of this olefin (56) furnished the di-O-isopropylidene derivative (57) which has the following spectral characteristics.



R = CH_3-$(CH_2)_{11}$-

Reagnets:- See Fig. 9

Fig. 10

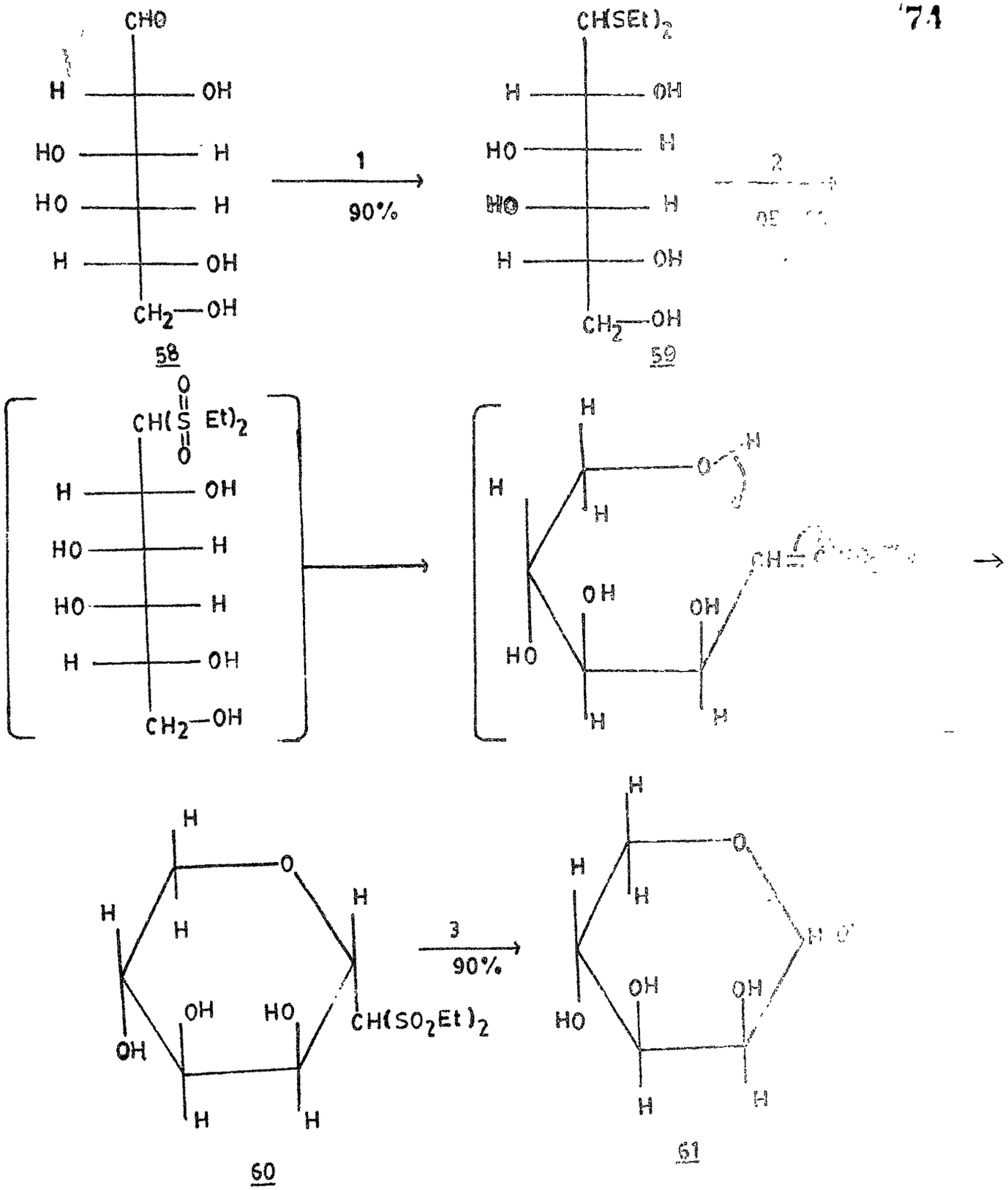
IR (Fig. 41) (CCl_4): gem-dimethyl 1386 cm^{-1} and 1376 cm^{-1}.
PMR (Fig. 42): O-C<u>H</u>,3H, bm, 3.9 ppm; O-C<u>H_2</u>, 2H, bm, 3.38 ppm.
Mass (Fig. 43): m/e 398 (M^+, 3.18%).

Hydrolysis of this di-O-isopropylidene (<u>57</u>) furnished D-arabino-1,2,3,4-octadecanetetrol. The structure was fully borne out by spectral data, (m.p. 136-137°).

3. <u>Towards the synthesis of D-lyxo-1,2,3,4-octadecanetetrol from D-lyxose.</u>

Synthesis of D-lyxo-1,2,3,4-octadecanetetrol was attempted in the similar lines as described for other isomers (Fig. 12).

D-lyxose was prepared from D-galactose by disulfone method[34] (<u>Fig. 11</u>). D-galactose-di-ethyldithioacetal was prepared in 90% yield from D-galactose, and was converted to disulfone (<u>60</u>) by treating it with peracetic acid in 95% yield. Disulfone (<u>60</u>) was treated with aq. ammonia for 7 days at 24° to furnish D-lyxose in 90% yield as a pale yellow syrup. D-lyxose di-ethyldithioacetal (<u>62</u>) was obtained by treating it with ethanethiol and aq. hydrochloric acid. Treatment of <u>62</u> with dry acetone and anhydrous ferric chloride furnished a complex mixture instead of the expected di-O-isopropylidene derivative. Other reagents like, anhydrous copper-sulfate, conc. sulfuric acid and phosphorous pentoxide

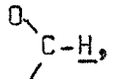


Reagents:- 1. $EtSH/H^+$, 2. AcO_2H, 3. aq.NH_3

Fig. 11

furnished products of similar nature. Since isopropylidenation of 62 failed, it was planned to prepare O-benzyl ethers derivative[35] of 62. When 62 was treated with benzyl chloride and sodium hydride[36] in DMSO, a complex mixture of products was formed, hence this method was not pursued further. When these two group protection reactions were failed, O-ethylidenation of 62 was tried. On treatment of 62 with paraldehyde and conc. sulfuric acid,[37] di-O-ethylidene-D-lyxosediethyldithioacetal mixture (62, Fig. 12) was formed. In this case, two geometrical isomers are possible, i.e., 2,3;4,5-, and 2,4;3,5-O-ethylidene derivatives and each, in turn will have two enantiomeric pairs. The structure of 63 was fully borne out by spectral data.

PMR (Fig. 15) ($CDCl_3$):



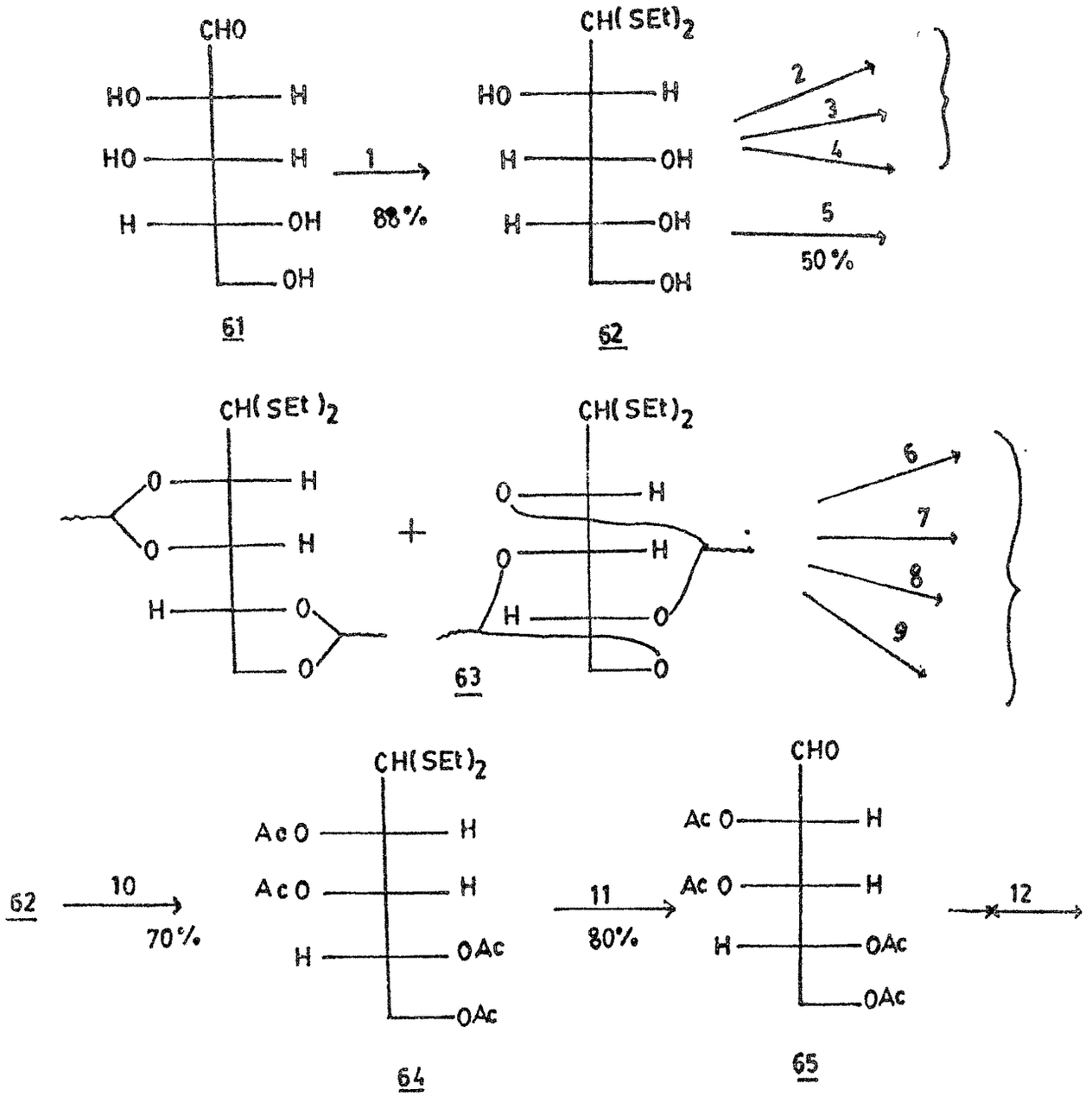
1H, bm, 4.72 ppm.

1H, bm, 4.92 ppm.

Mass (Fig. 46): m/e 308 (M^+, 66.3%).

The isomeric mixture, 63 was used in the next step without separating the isomers.

Regeneration of the aldehyde function from 63 was unsuccessful. The following reagents were tried for this purpose. Mercuric chloride/cadmium carbonate in aq. acetonitrile, thallium nitrate in methanol,[38] methyliodide



Reagents:- 1. EtSH/HCl, 2. $Me_2CO/FeCl_3$, 3. Me_2CO/anhy. $CuSO_4$, 4. BzCl/NaHDMSO, 5. Paraldehyde/H_2SO_4, 6. $HgCl_2$,$CdCO_3$/aq.MeCN, 7. $Tl(NO_3)_3$/MeOH, 8. MeI/Me_2CO,H_2O, 9. I_2,Me_2SO, 10. Ac_2O/Py, 11. Br_2/AcOH and 12. $CH_3(CH_2)_{12}Pph_3Br$/PhLi.THF.

Fig. 12

in aq. acetone[39], iodine in DMSO,[40] and sulfuryl chloride in methylene chloride.[41] Since regeneration of aldehyde group from 63 failed, it was planned to prepare aldehydo-D-lyxose tetraacetate[42] (66), a known aldehydo-D-lyxose derivative.

D-lyxosediethyldithioacetal-tetraacetate (64) was prepared by treating 62 with acetic anhydride and pyridine.[43] Regeneration of the aldehyde was achieved by treating 64 with Br_2 in acetic acid.[44] The resulting aldehyde (65) when subjected to Wittig reaction with tridecyltriphenylphosphorane failed to yield the required olefin.

E X P E R I M E N T A L

All m.ps and b.ps are uncorrected. Light petroleum refers to the fraction b.p. 60-80°. All solvent extracts were finally washed with water, brine and dried (Na_2SO_4). Solvents were evaporated under vacuo.

The following instruments were used for spectral/ analytical data: Perkin-Elmer Infrared Spectrophotometer, model 267; Perkin-Elmer model R32 (90 MHz) NMR spectrometer; Varian Mat CH_7 Mass spectrometer (70 eV, direct inlet system); Hewlett-Packard 5712A and 7624A gas chromatographs (Al columns, 180 cm x 0.6 cm; support, 60-80 mesh chromosorb W; carrier gas, H_2). All PMR spectra were taken in 15-20% soln in CCl_4 (unless stated to the contrary) with TMS as internal reference; signals are reported in ppm (δ); while citing PMR data the following abbreviations have been used: s(singlet), d(doublet), t(triplet), q(quartet), m(multiplet), br(broad), bm(broad multiplet). While summarising mass spectral data, besides the molecular ion, ten most abundant ions (m/e) are reported with their relative intensities. Optical rotations were measured on a Schmidt + Haendh electronic Polarimeter model Polatronic 1.

Silica gel for column chromatography (-100; + 200 mesh) was activated at 125-130° (6-8 hr) and then standardised,[45] Alumina for column chromatography was (-100 + 250 mesh)

activated at 400° (8-10 hr) and then standardised.[46] TLC was carried out on SiO_2-gel layers (0.25 mm) containing 15% gypsum and activated at 110-115° (2 hr).

All Wittig reactions were carried out in an atmosphere of dry N_2.

1,2;5,6-Di-O-isopropylidene-D-mannitol; 21

Fused zinc chloride (54 g, 0.39 mole) was added to dry acetone (270 ml), resulting turbid soln was cooled (25°) and decanted. This soln was added to D-mannitol (20, 34 g, 0.18 mole, finely powdered). The reaction mixture was stirred for 2 hr at 25°, filtered (recovering approximately 8 g of D-mannitol). The filtrate was added to a vigorously stirred soln of anhy. potassium carbonate (68g) in water (68 ml), covered over by anhy. ether (270 ml). Stirring was continued for 0.5 hr, after which the ether acetone soln was decanted and the zinc carbonate pellets were washed with acetone: ether mixture (1:1, 50 ml x 3). The combined solns were dried over anhy. potassium carbonate. Solvent evaporation under reduced pressure furnished 1,2;5,6-di-O-isopropylidene-D-mannitol (21)(20g, 65%), which was crystallized from water; m.p. 117-118° (lit.[11], m.p. 117-118°).

Pentadecylbromide

To a soln of palmitic acid (36 g, 0.14 mole) in dry carbontetrachloride (400 ml) was added red mercuric oxide (20.4 g, 0.09 mole). The reaction mixture was refluxed with stirring for 5 min. To this reaction mixture was added with stirring, bromine (30 g, 0.18 mole) in dry carbontetrachloride (20 ml) in 20-30 min, during which time refluxing was maintained. Refluxing and stirring continued for 1 hr, mercuric salts were filtered from the cooled reaction mixture. The clear filtrate was treated with aq. sodium hydroxide (5%, 100 ml). The ppt formed was filtered off. CCl_4 extract was separated from aq. soln, washed with water (50 ml x 3), brine and dried. Solvent evaporated under reduced pressure to yield pentadecylbromide, which was distilled (32 g, 80%), b.p. 135-140°/1 mm (lit.[12], b.p. 177°/10 mm) (98% purity by glc, 10% SE-30, 200°, Rt 20.5 min.).

PMR: $-CH_3$ (3H, bt, 0.91 ppm); $-CH_2$ (28H, s, 1.33 ppm); $Br-CH_2$ (2H, t, 3.39 ppm, J = 7Hz).

Pentadecyltriphenylphosphoniumbromide; 23

(a) By J. Cunnigham and R. Gigg's method.[12] Pentadecylbromide (1.2 g, 0.004 mole) and triphenylphosphine (1.08 g, 0.004 mole) were heated together at 140° for 5 hr. The mixture was cooled and dissolved in minimum quantity of acetone (5 ml), ether

was added to crystallize the product. No crystallization took place, all attempts to crystallize the glassy products were failed.

(b) By refluxing in benzene or toluene[13]. Pentadecylbromide (1.2 g, 0.004 mole) and triphenylphosphine (1.08 g, 0.004 mole) were refluxed in benzene (or toluene, 30 ml) for 12 hr. Solvent removal furnished a glassy material which on treatment with dry ether did not crystallize. All attempts to crystallize this material were failed.

(c) By refluxing in acetonitrile.[13] Pentadecylbromide (15.7g, 0.054 mole) and triphenylphosphine (14.4 g, 0.056 mole) were refluxed in acetonitrile (200 ml) for 12 hr. Acetonitrile was distilled off and the residue was triturated with dry ether (100 ml) and cooled (0-10°) to give white solid (23) which was filtered under N_2 atmosphere, washed with dry ether (25 ml x 2), dried (24.5 g, 80%), m.p. 89-90° (lit.[12], m.p. 92°).

2,3-O-Isopropylidene-D-glyceraldehyde,[11] 22

To a stirred soln of lead tetraacetate (4.4 g, 0.01 mole) in dry benzene (80 ml), was added 1,2; 5,6-di-O-isopropylidene-D-mannitol (21, 2.6 g, 0.01 mole). After stirring for 40 min at 25°, anhy. potassium carbonate (10 g) was added, and stirred for 5 min. This clear soln containing

2,3-O-isopropylidene-D-glyceraldehyde was used in the Wittig reaction immediately without isolating 22.

1,2-O-Isopropylidene-cis-1,2-octadec-3-ene diol; 24

To a stirred suspension of pentadecyltriphenylphosphonium bromide (11.06 g, 0.02 mole) in dry ether (120 ml), etherial soln of phenyl lithium (20 ml of 1 molar soln; 1.68 g, 0.02 mole) was added dropwise. Resulting red coloured soln was refluxed for 5-10 min, cooled (10-15°), and filtered to remove lithium salts which were formed during the reaction. To this red coloured soln, 2,3-O-isopropylidene-D-glyceraldehyde (22) in benzene (from above LTA cleavage reaction) was added dropwise. The resulting colourless reaction mixture was refluxed for 6 hr (throughout the reaction, complete anhydrous and inert atmosphere was maintained). Solvent evaporated, the residue was diluted with water (200 ml), and extracted with light petroleum (100 ml x 3). The combined extract was washed with water (50 ml x 3), brine and concentrated. The concentrate was chromatographed on SiO_2-gel/ IIB column (1.7 cm x 64 cm). While monitoring with Tlc (solvent, 20% ether in pet ether), the following pooled fractions were collected:

Fraction 1	pet ether	50 ml x 2	alkane, imourity
Fraction 2	pet ether	50 ml x 2	alkane, imourity

Fraction 3	pet ether	10 ml x 3	0.05 g, impurity + 24, R_f 0.55
Fraction 4	pet ether	10 ml x 4	0.5 g R_f 0.55, (liquid)
Fraction 5	10% EtOAc/ pet ether	10 ml x 10	2.5 g, R_f 0.55
Fraction 6	EtOAc	10 ml x 4	polar material

Fractions 4 and 5 were pooled and distilled, b.p. 185-190°(bath)/0.1 mm and identified as 1,2,-O-isopropylidene-cis-1,2-octadece-3-nediol (24).

$[\alpha]_D$ + 14° (c, 0.2%, EtOH).

IR (Fig. 13) (Neat): 3000, 3940, 2860, 1660, 1472, 1385, 1375, 1255, 1220, 1162, 1065 and 865 cm^{-1}.

PMR (Fig. 14): C-C$\underline{H}_3$ (3H, bt, 0.89 ppm); C$\underline{H}_2$ and $C(\underline{CH}_3)_2$ (30H, bs, 1.26 ppm); O-C$\underline{H}_2$ (1H, dd, 3.36 ppm, J_{gem} = 8 Hz, J_{vic} = 6 Hz; 1H, dd, 3.92 ppm; J_{gem} = 8 Hz, J_{vic} = 6Hz); C = C - C(O) - $\underline{H}$ (1H, m, 4.7 ppm); C=C-$\underline{H}$ (2H, m, 5.4 ppm).

Mass (Fig. 15): m/e 324 (M^+, 8.16%), 309 (42.8%), 266 (27.2%), 137 (19.72%), 123 (36.7%), 109 (60.54%), 97 (100%), 95 (87.75%), 83 (82.9%), 81 (84.35%) and 55 (80.27%).

(Found C, 77.25; H, 12.02. $C_{21}H_{40}O_2$ requires C, 77.77; H, 12.34%).

cis-1,2-Octadec-3-enediol; 25

To a stirred soln of 24 (2.5 g) in dioxane (50 ml), $HClO_4$ aq. soln (10%, 10 ml) was added at 25° and stirring continued for 5 hr. Diluted with water (100 ml), extracted with EtOAc (100 ml x 3), washed with water (50 ml x 3), brine and dried. Solvent evaporated under vacuo to furnish 25 (2.2 g, m.p. 54°) which was crystallized from acetonitrile, m.p. 58-59° (1.98 g, 90% yield), $[\alpha]_D$ - 32° (c, 1.1%, EtOH); R_f 0.21 (Tlc, 1:2;: pet ether: ether).

IR (Fig. 16) (KBr-pellet): 3320, 2910, 2845, 1464, 1312, 1088, 1065, 1020, 872 and 710 cm^{-1}.

PMR (Fig. 17) ($CDCl_3$): C-C$\underline{H}_3$ (3H, bt, 0.9 ppm); C$\underline{H}_2$ (24H, s, 1.28 ppm); O-C$\underline{H}_2$ (2H, b, 3.48 ppm); O-C$\underline{H}$ (1H, bm, 4.5 ppm); C=C-$\underline{H}$ (2H, bm, 5.42 ppm).

Mass (Fig. 18): m/e 253 (M^+-31, 8.8%); 236 (4.4%), 137 (2.2%), 109 (28.8%), 95 (62.22%), 83 (44%), 81 (62.2%), 67 (44%), 57 (100%), and 55 (68.8%).

(Found C, 75.28; H, 12.12. $C_{18}H_{36}O_2$ requires C, 76.05; H, 12.65%).

1,2-O-Isopropylidene-cis-1,2-octadecene diol (24) from 25

To a stirred soln of cis-octadec-3-ene diol (25, 1.8 g) in dry acetone (180 ml), was added anhyd. ferric chloride,

(0.6 g) at 0-5° and stirred for 1 hr at 25°. Diluted with aq. potassium carbonate (10%, 20 ml). Acetone was evaporated, the residue extracted with chloroform (20 ml x 3) washed with water (20 ml x 3), dried and evaporated to furnish yellowish liquid 1,2-O-isopropylidene-cis-1,2-octadece-3-ne diol (24, 1.9 g).

D-Arabino-, and D-xylo-1,2,3,4-octadecane-tetrols; 28 and 27

To a stirred soln of 24 (0.972 g, 0.003 mole) in formic acid (85%, 1.8 ml) at 10°, aq. Hydrogenperoxide (10%, 0.5 ml, 0.004 mole) was added dropwise and stirred at 25° for 12 hr. Formic acid and water were removed under vacuo (40°), an ice cold aq. NaOH (50%, 1 ml) was added to the residual viscous mixture and stirred at 40-45° for 1 hr. It was diluted with water (10 ml, extracted with EtOAc (10 ml x 4), washed with water (10 ml x 3), brine, dried and solvent evaporated under vacuo to furnish sticky solid (0.85 g, 90%), which was dissolved in absolute alcohol (6 ml) and kept at 25° for 12 hr. Fine needles of D-arabino-1,2,3,4-octadecanetetrol crystallizes out (0.13 g, 15%), m.p. 136-37°. Recrystallized from absolute alcohol, m.p. 136-137°. $[\alpha]_D$ + 50° (c, 0.05% EtOH). R_f 0.6 (Tlc, 20% MeOH in EtOAc).

IR (Fig. 19 (KBr-pellet): 3350, 3245, 2920, 2840, 1460, 1406, 1255, 1110, 1076, 1036, 874 and 715 cm^{-1}.

Mass (Fig. 20): m/e 269 (M^+-49, 2%), 258 (2%), 225 (2%), 137 (2%), 125 (2%), 125 (41%), 74 (100%), 69 (41.6%), and 67 (20.8%).

(Found C, 67.46; H, 11.93. $C_{18}H_{38}O_4$ requires C, 67.88; H, 12.03%).

The mother liquor was kept at 20° for 24 hr, furnished crystalline solid D-xylo-1,2,3,4-octadecanetetrol (0.33 g, m.p. 80-81°) which was crystallized from absolute alcohol (0.28 g, 30%), m.p. 83-84°. $[\alpha]_D$ + 10° (c, 0.11%, EtOH). R_f 0.6 (Tlc, 20% MeOH in EtOAc).

IR (Fig. 21) (KBr-pellet): 3420, 3320, 2920, 2850, 1465, 1134, 1070, 930, 905, 860, 850, and 712 cm^{-1}.

PMR (Fig. 22) (DMSO-D_6): C-C$\underline{H}_3$ (3H, b, 0.91 ppm); C$\underline{H}_2$ (26H, s, 1.28 ppm); O-C$\underline{H}_2$ (2H, b, 3.45 ppm); O-C$\underline{H}$ (1H, bm, 3.75 ppm, 1H, bm, 3.94 ppm, and 1H, bm, 4.25 ppm).

Mass (Fig. 23): m/e 319 (M^++ 1, 1%), 275 (1%), 225 (2%), 123 (2%), 97 (10%), 95(12%), 85 (8%), 81 (14%), 74 (100%), 69 (34%).

(Found C, 67.48; H, 11.80. $C_{18}H_{38}O_4$ requires C, 67.88; H, 12.03%).

D-Ribo-1,2,3,4-octadecanetetrol; 31

To a stirred soln of olefin (24, 0.324 g, 0.001 mole) and osmiumtetroxide (0.088 g, 0.00023 mole) in aq. THF (20%, 10 ml), was added aq. sodium chlorate (0.16 g, 0.0013 mole in 2 ml water) dropwise at 25°C, stirring continued for 3 hr, diluted with water (20 ml), extracted with EtOAc (20 ml x 3), washed with water (20 ml x 3), brine treated with activated carbon to remove the colour. Solvent evaporation furnished the viscous liquid (0.32 g) which was treated with aq. $HClO_4$ (10%, 2 ml) in dioxane (10 ml) for 1 hr. Diluted with water (20 ml) extracted with EtOAc (20 ml x 3), washed with water (20 ml x 3), brine, dried and evaporated to furnish the crude product (0.3 g) which was chromatographed on SiO_2-gel/IIB column (1.6 cm x 35 cm). While monitoring with Tlc (solvent, 20% MeOH in EtOAc), the following pooled fractions were collected:

Fraction 1	EtOAc	25 ml x 6	0.2 g, viscous liquid R_f 0.8.
Fraction 2	EtOAc	25 ml x 6	0.06 g, solid material R_f 0.65
Fraction 3	EtOAc	25 ml x 2	-

Fraction 2 (0.06 g; 15%) was crystallized from absolute alcohol to furnish needles of D-ribo-1,2,3,4-octadecanetetrol,

m.p. 116-117°. $[\alpha]_D$ - 8.86° (c, 0.44%, EtOH); R_f 0.65 (Tlc 20% MeOH in EtOAc).

IR (Fig. 24) (KBr-pellet): 3420, 3350, 2920, 2850, 1465, 1215, 1068, 1040, 1020, and 714 cm^{-1}.

PMR (Fig. 25) (DMSO-D_6): C-C$\underline{H}_3$ (3H, bt, 0.9 ppm); C$\underline{H}_2$ (26H, s, 1.28 ppm); O-C$\underline{H}_2$ (2H, b, 3.5 ppm), O-C$\underline{H}$ (2H, d, 4.2 ppm, 1H, b, 4.4 ppm).

Mass (Fig. 26): m/e 284 (M^+-34, 11.9%), 264 (19.4%), 257 (10.6%), 256 (58.6%), 213 (13.3%), 129 (26.6%), 111 (19.9%), 98 (25.3%), 97 (43.9%), 73 (73.3%) and 55 (100%).

(Found C, 67.43; H, 11.96. $C_{18}H_{38}O_4$ requires C.67.88; H, 12.03%).

D-Ribose diethyldithioacetal; 38

To a stirred soln of D-ribose (37, 5 g, 0.03 mole) in ice cold hydrochloric acid (aq. 35%, 5 ml) ethanethiol (10 ml, 0.13 mole) was added and stirred at 0-5° for 0.5 hr and further 6 hr at 25°. Diluted with methanol (20 ml) and neutralized with lead carbonate. The unsoluble lead salts were filtered off and washed thoroughly with boiling methanol (125 ml x 3). The combined solvent was removed under vacuo to furnish the crude product (8 g, m.p. 75-78°), crystallized from ethanol to give needles of D-ribose diethyldithioacetal (38, 6.62 g,

80%), m.p. 82-83° (lit.[32], m.p. 82-83°); $[\alpha]_D$ - 39° (c, 0.5%, H_2O) lit.[32], $[\alpha]_D$ -41° (c, 0.5%, H_2O) . R_f 0.44 (Tlc, 4% MeOH in EtOAc).

Mass: m/e 256 (M^+, 7.6%), 185 (3.8%), 184 (3.8%), 177 (15.38%), 135 (100%), 107 (23.0%), 105 (42.3%), 75 (38.4%), 73 (28.8%) and 61 (26.9%).

2,3;4,5-and 2,4;3,5-Di-O-isopropylidene-D-ribose-diethyl-dithio acetals; 39

a) Using anhy. copper sulfate[29]. D-Ribosediethyldithioacetal (1 g), dry acetone (30 ml) and anhydrous copper sulfate (5.0 g) were stirred for 36 hr at 25°. The suspension was filtered through Celite pad and the pad washed repeatedly with acetone (10 ml x 3). The filtrate was evaporated to a syrup (1.2 g), chromatographed on neutral alumina/IIB (1.7 cm x 18 cm). While monitoring by Tlc, the following pooled fractions were collected (solvent, 20% EtOAc/C_6H_6).

Fraction 1	pet ether	250 ml x 2	0.4 g, viscous liquid, R_f 0.5
Fraction 2	pet ether	250 ml x 5	0.4 g, R_f 0.5
Fraction 3	MeOH	60 ml	polar material.

Fraction 1 and 2 were pooled and identified as 39 by spectral data.

$[\alpha]_D$ -55° (c, 0.8%, $CHCl_3$) lit.[32], -53° (c, 0.8%, $CHCl_3$) .
98% purity by glc, 10% SE-30, 200°, Rt. 10.5 min. (2,3;4,5-isomer, 65%), 13 min (2,4;3,5-isomer, 35%) [29].

PMR: C-CH_3 (18H, m, 1.36 ppm), S-CH_2 (4H, bm, 2.7 ppm), O-CH_2, O-CH (5H, bm, 4.0 ppm) and S-CH (1H, bm, 4.8 ppm).

Mass: m/e 336(M^+, 38%), 321 (6%), 275 (9%), 263 (7%), 217 (84%), 203 (6%), 201 (6%), 177 (7%), 159 (30%), 143 (100%), 135 (96%), 101 (30%) and 59 (44%).

b) Using ferric chloride (anhydrous)[31]

To a stirred soln of D-ribose-diethyldithioacetal (1 g) in dry acetone (100 ml) at 0-5°, anhy. ferric chloride (0.3 g) was added and stirred for 1 hr at 25°. Potassium carbonate aq. soln (10%, 10 ml) was added and solvent evaporated. The residue was extracted with chloroform (10 ml x 3), washed, dried and evaporated to give crude 39 (1.29 g), which was chromatographed on neutral alumina column (1.7 cm x 18 cm). While monitoring by Tlc, the following pooled fractions were collected:

Fraction 1.	pet ether	250 ml x 3	0.6 g, R_f 0.5
Fraction 2	pet ether	250 ml x 4	0.42 g, R_f 0.5
Fraction 3	pet ether	250 ml x 2	0.02 g, R_f 0.5
Fraction 4	MeOH	40 ml	70 mg, polar material .

Fractions 1,2 and 3 were identified as 39 (1.04 g, 80%) by spectral data. 98% purity by glc, 10% SE-30, 200° R_t 10.5 min (2,3;4,5-isomer, 65%), 13 min (2,4;3,5-isomer, 35%).

2,3;4,5-and 2,4;3,5-Di-O-isopropylidene-aldehydo-D-ribose;40

To a stirred soln of 39 (0.336 g) and cadmium carbonate (1.7 g) in aq. acetonitrile (20%, 21 ml), was added mercuric chloride soln (1.7 g in 20% aq. acetonitrile, 7 ml) dropwise, stirred for 6 hr at 25°. Mercuric salts were filtered off and the filtrate was diluted with potassium carbonate aq. soln (1%, 15 ml), extracted with chloroform (15 ml x 3), washed, dried and evaporated to give crude aldehyde which was distilled to furnish 40 (0.19 g, 85%), b.p. 70-75°(bath)/0.1 mm (lit.[32], b.p. 73-75°/0.1 mm), $[\alpha]_D$-30 (c, 0.6%, $CHCl_3$) lit.[32], $[\alpha]_D$-36 (c, 0.6%, $CHCl_3$). R_f 0.52, 0.32 (Tlc, 20% EtOAc in benzene).

PMR: C-C$\underline{H}_3$ (12H, 2 bs, 1.4 ppm and 1.53 ppm); OC$\underline{H}_2$, O-C$\underline{H}$ (5H, bm, 4.0 ppm), O=C-$\underline{H}$ (1H, d, 9.62 ppm).

Mass: m/e 215 (M^+-15, 8.3%), 171 (4.9%), 157 (5.8%), 143 (9%), 115 (10.8%), 101 (18.3%), 85 (18.3%), 59 (37.5%) and 43 (100%).

Tridecyl bromide; 42

This compound (32 g) was prepared from 41 in the same manner as described for pentadecyl bromide in 80% yield. b.p. 150-155°/10 mm (lit.[14], 148-9/9.5 mm). (98% purity by glc, 10% SE-30, 200°. Rt 4.10 min).

Tridecyltriphenylphosphonium bromide, 43

This compound (43, 11 g) was prepared in 80% yield in the similar lines as described for 23, m.p. 83-85° (lit.[2], m.p. 84-86°).

1,2;3,4-, and 1,3;2,4-Di-O-isopropylidene D-ribo-1,2,3,4-octadec-5-enetetrol; 44

To a stirred soln of tridecyltriphenylphosphonium bromide (43, 0.372 g, 0.71 mmole) in dry THF (5 ml) was added ethereal soln of phenyllithium (0.75 ml of 1 molar soln, 0.6 mg, 0.73 mmole). Resulting red coloured soln was stirred and refluxed for 5-10 min, cooled (10-15°). To this cooled soln, freshly prepared aldehydo-ribo-diacetonide (40, 0.16 g, 0.69 mmole) in dry THF (2 ml) was added dropwise and refluxed for 6 hr. The reaction mixture was cooled, solvent evaporated, diluted with water (10 ml) extracted with pet ether (5 ml x 3), washed with water (5 ml x 2), brine and dried. It was concentrated under reduced pressure. The concentrate was

chromatographed on alumina column (neutral/IIB, 14.5 cm x 1.7 cm). While monitoring with Tlc (solvent, 25% ether in pet ether), the following fractions were collected:

Fraction 1	pet ether	50 ml x 1	0.03 g, hydrocarbon inourity.
Fraction 2	25% benzene in pet ether	15 ml x 15	0.16 g viscous liquid. R_f 0.5, 0.42

Fraction 2 (0.16 g, 60%) was identified as 44, $[\alpha]_D$ - 91.2 (c, 0.25%, EtOH).

IR (Fig. 27) (Neat): 2984, 2920, 2855, 1658, 1460, 1380, 1370, 1245, 1218, 1165, 1070, 1045, 875 and 850 cm^{-1}.

PMR (Fig. 28): C-C$\underline{H}_3$ (3H, bt, 0.88 ppm); C=C-C$\underline{H}_2$ (2H, bm, 2.06 ppm; C$\underline{H}_2$, $C(\underline{C}H_3)_2$ (32H, bs, 1.3 ppm).

O-C$\underline{H}$, O-C$\underline{H}_2$ (5H, 3 bm, 3.95 ppm, 4.40 ppm and 4.86 ppm).

Mass (Fig. 29): m/e 396 (M^+, 2%), 381 (10%), 323 (5%), 266 (35.9%), 251 (25%), 237 (25%), 157 (10.7%), 114 (15.7%), 101 (100%), 97 (67.85%), 83(25%), and 59 (47.17%).

(Found C, 72.38%; H, 10.69. $C_{24}H_{44}O_4$ requires C. 72.73; H, 11.11%).

1,2;3,4-1,3;2,4-Di-isopropylidene-D-ribo-1,2,3,4-octadecanetetrol; 45

The compound 44 (0.15 g) in absolute alcohol (10 ml) was hydrogenated at 25°/1 atm in presence of 10% palladium-charcoal until the calculated quantity of hydrogen had been consumed. Filtration and solvent evaporation furnished 45 (0.15 g) as viscous liquid.

$[\alpha]_D$ - 94.5° (c, 0.25% in EtOH).

R_f, 0.52 and 0.42 (Tlc, 25% ether in pet ether).

IR (Fig. 30) (CCl_4): 3010, 2950, 2880, 1475, 1460, 1385, 1375, 1260, 1225, 1164, 1075 and 888 cm^{-1}.

PMR (Fig. 31): C-C$\underline{H}_3$ (3H, bt, 0.9 ppm); C$\underline{H}_2$, C$(\underline{CH}_3)_2$ (36H, bs, 1.3 ppm); O-C$\underline{H}$, O-C$\underline{H}_2$ (5H, 2 bm, 3.55 ppm and 3.88 ppm),

Mass (Fig. 32): m/e 398 ($M^{+\cdot}$, 1.3%), 384 (16%), 383 (61.3%), 297 (100%), 298 (22.6%), 157 (6.6%), 143 (10.6%), 109 (14.6%), 101 (77.3%), 85 (19.9%), 81 (19.9%), 69 (34.6%), 59 (70.6%) and 57 (42.6%).

(Found, C, 72.42; H, 11.25. $C_{24}H_{46}O_4$ requires C, 72.36; H, 11.55%).

D-Ribo-1,2,3,4-octadecanetetrol; 31

Compound 45 (0.1 g) was stirred in dioxane (10 ml) and aq. $HClO_4$ soln (10%, 3 ml) at 25° for 2 hr, diluted with water (100 ml), extracted with EtOAc (25 ml x 3), washed, dried and evaporated to furnish 31 (0.08 g) which was crystallized from

absolute alcohol, m.p. 115-117°, $[\alpha]_D$ - 8.86 (c, 0.44% EtOh).

D-xylose diethyldithioacetal; 47

Compound 47 (7 g) was prepared from X-xylose (5 g) in 82% yield, in a similar way as described for D-ribose diethyldithioacetal. m.p. 63-65° (lit.[32], m.p. 63-65°), $[\alpha]_D$ - 30 (c, 0.5% water), (lit.[32], $[\alpha]_D$ - 30 (water), R_f 0.55 (Tlc 20% MeOH in EtOAc).

Mass: m/e 256 (M^+, 19.9%), 185 (6.3%), 177 (7.9%), 135 (100%), 107 (43.3%), 105 (63.3%), 75 (35.3%) and 61 (42.6%).

2,3;4,5-O-Disopropylidene-D-xylose diethyldithioacetal; 48

Compound 48 (5.5 g) was prepared from 47, using anhy. ferric chloride in a similar way as described for 40 in 85% yield. (98% ourity by glc, 10% SE-30, 200°, R_t, 12 min.). $[\alpha]_D$ - 50 (c, 0.3% benzene) (lit.[32], $[\alpha]_D$ - 51.2 (c, 0.29% benzene). R_f 0.5 (Tlc, 20% EtOAc in benzene).

PMR: $-CH_3$ (18H, m. 1.4 ppm); $S-CH_2$ (4H, m, 2.75 ppm), $O-CH$, $O-CH_2$ (5H, bm, 3.9 ppm) $S-CH$ (1H, bm, 4.25 ppm).

Mass: m/e 336 (M^+, 21.05%), 321 (3.1%), 275 (4.2%), 263 (3.1%), 201 (19.9%), 159 (26.3%), 143 (59.9%), 135 (100%) and 101 (63.15%).

2,3;4,5-Di-O-isopropylidene-aldehydo-D-xylose; 49

Compound 49 (0.48 g) was prepared in the similar lines as described for 41 in 70% yield. B.p. 75-80°/0.1 mm $[\alpha]_D$ - 28° (c, 3.1%, EtOH) Lit.[47], $[\alpha]_D$-23° (c, 3.0%, EtOH). R_f 0.32 (Tlc, 20% EtOAc in C_6H_6). (98% purity by glc, 10% SE-30, 170°, R_t, 3.2 min).

pMR: CH_3 (12H, 3s, 1.33, 1.37, 1.44 ppm), O-CH, $O-CH_2$ (5H, m, 4 ppm); O=C-H (1H, d, 9.7 ppm, J = 2Hz).

1,2;3,4-Di-O-isopropylidene-D-xylo-1,2,3,4-Octadec~~a~~5-enetetrol;50

Compound 50 (0.7 g) was prepared in the similar lines as described for 44 in 60% yield. The pet ether concentrate was chromatographed on alumina (neutral IIB) column (1.7 cm x 36 cm), while monitoring with Tlc (solvent, 2~5% ether in pet ether).

Fraction 1	pet ether	50 ml x 4	-
Fraction 2	25% benzene in pet etner	50 ml x 14	700 mg, viscous liauid, R_f 0.5.
Fraction 3	benzene	50 ml x 2	Polar material.

Fraction 2 (0.7 g) was identified as 50. $[\alpha]_D$-30.5° (c, 0.28%, EtOH).

IR ((Fig. 33) (CCl_4): 2945, 2875, 1625, 1385, 1375, 1265, 1220, 1162, 1075 and 1030 cm^{-1}.

PMR (Fig. 34): $C-CH_3$ (3H, bt, 0.89 ppm), CH_2, $C(CH_3)_2$.

(32H, 3s, 1.25, 1.32 and 1.36 ppm); O-C$\underline{H}_2$ (1H, dd, 3.45 ppm J_{gem} = 8 Hz; J_{vic} = 2Hz; 1H, merged with O-C$\underline{H}$,2H; 3.89 ppm); C=C-C$\underline{H}$-O (1H, t, 4.7 ppm, J = 8 Hz); $\underline{H}$C=C$\underline{H}$ (2H; bm, 5.5 ppm).

Mass (Fig. 35): m/e 396 (M^+, 5.7%), 387 (24.1%), 266 (54.02%), 251 (25.28%), 237 (25.28%), 183 (11.49%), 157 (25.28%), 105 (36.78%), 101 (100%), 91 (67.8%) and 59 (43.67%).

(Found C, 73.11; H, 10.76. $C_{24}H_{44}O_4$ requires C, 72.73; H, 11.11%).

1,2;3,4-Di-O-isopropylidene-D-xylo-1,2,3,4-octadecanetetrol; 51

Compound 50 (0.5 g) was hydrogenated over palladium-charcoal (10%) as described for 44 to furnish 51 in quantitative yield, as viscous liquid. $[\alpha]_D$ - 34.21 (c, 0.2%, EtOH), R_f 0.52 (Tlc, 25% ether in pet ether). IR (Fig. 36) (CCl_4): 2945, 2878, 1385, 1375, 1265, 1220, 1164, 1080 amd 1020 cm^{-1}.

PMR (Fig. 37): C-C$\underline{H}_3$ (3H, bt, 0.9 ppm); C$\underline{H}_2$, C$\begin{smallmatrix} \diagup \underline{CH}_3 \\ \diagdown \underline{CH}_3 \end{smallmatrix}$ (38H, 2s, 1.25, 1.3 ppm); O-C$\underline{H}_2$ (1H, dd, 3.50 ppm; J_{gem} = 8 Hz), J_{vic} = 2Hz; 1H, merged with O-C$\underline{H}$ signal, 3.9 ppm); O-C$\underline{H}$ (3H, m, 3.9 ppm).

Mass (Fig. 38): m/e 398 (M^+, 4.63%), 384 (25.16%), 383 (98.67%), 325 (23.84%), 323 (16.5%), 297 (100%), 265 (17.8%), 101 (31.78%), and (29.8%).

(Found. C, 72.26; H, 11.07. $C_{24}H_{46}O_4$ requires C, 72.36; H, 11.55%).

D-xylo-1,2,3,4-octadecanetetrol; 27

Compound 27 (0.10 g) was obtained from 51 in a similar way as described for 31. D-xylo-1,2,3,4-octadecanetetrol was crystallized from absolute alcohol. m.p. 83-84°, $[\alpha]_D$ + 10 (c, 0.011%, EtOH).

D-Arabinose diethyldithioacetal; 53

To a stirred soln of D-arabinose (4 g, 0.024 mole) in aq. hydrochloric acid (35%, 4 ml) at 0-5°, was added ice cold ethanethiol (8 ml, 0.104 mole). Stirring continued for 0.5 hr. After the usual work-up, 53 was crystallized from absolute alcohol (6 g, 90%), m.p. 125-126° (lit.[33], m.p. 125-126°), $[\alpha]_D$ -11.0 (c, 0.5%, MeOH) lit.[33], $[\alpha]_D$-11.0 (c, 5.0%, MeOH) . R_f 0.54 (Tlc, 20% MeOH in EtOAc).

2,3;4,5-Di-O-isooropylidene-D-arabinosediethyldithio acetal; 54

To a stirred soln of D-arabinosediethyldithioacetal (4 g) in dry acetone (400 ml) at 0-5°, anhy. ferric chloride (1.2 g) was added and stirred for 3 hr at 25°. K_2CO_3 aq. soln (10%, 40 ml) was added, solvent evaporated, extracted with chloroform (40 ml x 3), washed, dried and evaporated to furnish 54 (4.85 g) in 92% yield. (98% purity by Glc, 10% SE-30, 200°, Rt 12.5 min). $[\alpha]_D$ + 80.0 (c, 1.4%, MeOH) (lit.[33], $[\alpha]_D$ + 83.3 (c, 1.4%, MeOH) . R_f, 0.52 (tlc, 20% EtOAc in C_6H_6).

PMR: -C$\underline{H}_3$ (18H, m, 1.36 ppm), C$\underline{H}_2$ (4H, m, 2.7 ppm), O-C$\underline{H}_2$, O-C$\underline{H}$ (5H, m, 3.96 ppm), S-C$\underline{H}$ (1H, bm, 4.15 ppm).

2,3;4,5-Di-O-isopropylidene-aldehydo-D-arabinose 55

Compound 55 (0.16 g) was obtained from 54 in the similar lines as described for 40 in 70% yield, b.p. 65-70(bath)/0.3 mm (lit.[48], b.p. 60-80°/0.3 mm). $[\alpha]_D$-16° (c, 4.5% $CHCl_3$) lit.[48] $[\alpha]_D$-17.1° (c, 7.1%, $CHCl_3$) . (98% ourity by glc, 10% SE-30, 170°, Rt, 3.5 min.).

PMR: C$\underline{H}_3$ (12H, 4s, 1.29, 131, 1.35 and 1.41 ppm), O-C$\underline{H}_2$, O-C$\underline{H}$ (4H, m, 4 ppm), OHC-C$\underline{H}$ (1H, b, 4.26 ppm); O=C-$\underline{H}$ (1H, d, 9.60 ppm).

Mass: m/e 215 (M^+-15, 28.75%), 201 (11.25%), 181 (1.25%), 143 (31.25%), 101 (37.5%), 85 (36.25%), 59 (35%) and 43 (100%).

1,2;3,4-Di-O-isopropylidene-D-arabino-1,2,3,4-octadec-5-enetetrol 56.

This compound 56 (0.16 g) was prepared in 60% yield from 55 as described for 44. The pet ether concentrate was chromatographed on neutral alumina/IIB column (1.7 cm x 14.5 cm). While monitoring with Tlc (solvent, 25% ether in pet ether), the following pooled fractions were collected.

Fraction 1	pet ether	50 ml x 1	0.03 g hydrocarbon imourity.
Fraction 2	25% benzene in pet ether	15 ml x 20	0.16 g, viscous liquid, R_f 0.54.
Fraction 3	benzene	15 ml x 3	oolar material.

Fraction 2 (0.16 g) uas identified as 55, $[\alpha]_D^c$ -35.2 (c, 0.25%, EtOH).

IR (Fig. 39) (CCl_4): 3010, 2945, 2875, 1630, 1460, 1385, 1375, 1220, 1065, and 855 cm^{-1}.

PMR (Fig. 40): C-C$\underline{H}_3$ (3H, b, 0.9 ppm); C$\underline{H}_2$, $C(\underline{CH}_3)_2$ (32H, 2s, 1.26 and 1.32 opm); O-C$\underline{H}_2$, O-C$\underline{H}$ (4H, 2 m, 3.55 and 4 ppm). C=C-C$\underline{H}$-O (1H, t, 4.56 opm, J = 7 Hz), $\underline{HC}$=C$\underline{H}$ (2H, m, 5.92 opm).

(Found. C, 72.34; H, 1070. $C_{24}H_{44}O_4$ requires C, 72.73%, H, 11.11%).

1,2;3,4-Di-O-isopropylidene-D-arabino-1,2,3,4-octadecanetetrol, 57.

Comoound 56 (0.15 g) was hydrogenated as described earlier for 44, to furnish 57 as viscous liquid in quantitative yield. $[\alpha]_D^e$ -42 (c, 0.2%, EtOH).

IR (Fig. 41) (CCl_4): 3010, 2950, 2875, 1475, 1460, 1386, 1376, 1220, 1160, 1065 and 855 cm^{-1}.

PMR (Fig. 42): C-C$\underline{H}_3$ (3H, b, 0.9 ppm); C$\underline{H}_2$, C$\begin{smallmatrix}\diagup\underline{CH}_3\\ \diagdown\underline{CH}_3\end{smallmatrix}$ (38H, bs, 1.3 ppm), O-C$\underline{H}_2$ (2H, bm, 3.38 ppm), O-C$\underline{H}$ (3H, bm, 3.9 ppm).

Mass (Fig. 43): m/e 398 (M^+, 3.18%), 383 (100%), 325 (5.1%), 297 (9.9%), 265 (7.0%), 157 (12.7%), 109 (9.5%), 101 (56.0%), 69 (21.01%), 59 (50.91%) and 57 (25%).

(Found. C, 72.38; H, 11.19; $C_{24}H_{46}O_4$ requires C, 72.36; H, 11.55%).

D-Arabino-1,2,3,4-octadecane-tetrol; 28

Compound 57 (0.1 g) was hydrolyzed as described earlier to give 28 (0.07 g) which was crystallized from absolute alcohol, m.p. 136-137°; $[\alpha]_D$ + 50 (c, 0.5%, EtOH).

D-Galactosediethyldithioacetal; 59

Compound 59 (14 g) was prepared from D-galactose in the similar way as described for 38 in 90% yield. m.p. 140-142° (lit.[34], m.p. 140-43°).

D-galactose disulfone; 60

To a stirred and cooled (0-5°) soln of 59 (10 g, 0.035 mole) in methanol (500 ml) was added peracetic acid (40%, 50.0 ml) at 0-5°, stirring continued for 24 hr at 10-15°. Solvent evaporated under vacuo using rotovapour. The crude product was crystallized

from absolute alcohol to furnish 60 (10.5g, 95%), m.p. 190-93° (lit.[34], m.p. 193-95°).

D-Lyxoso; 61 . Disulfone (60 , 10 g) was stirred in aq. ammonia (200 ml, pH 10-11) at 24° for 7 days. After filtration, the soln was deionised with Amberlyst-15 and Amberlite-35 (OH form) and then extracted continuously with chloroform for 12 hr to remove diethyl sulfonyl methane. On concentration, a pale yellow syrup of D-lyxose (4.2 g, 93%) was obtained.

D-Lyxose diethyldithioacetal; 62

62 (1.5 g) was prepared as described for 38 in 88% yield. Crystallized from absolute alcohol, m.p. 103-104° (lit.[43], m.p. 104°), $[\alpha]_D$ + 25 (c, 0.5%, EtOH) lit.[43], $[\alpha]_D$ + 20 (EtOH) .

Di-O-isopropylidenation of 62

(a) Using anhy. ferric chloride. Compound 62 (0.5 g) was treated with dry acetone and anhy. ferric chloride as described for 38. The product was a complex mixture (Tlc).

(b) Using anhyd. copper sulfate. Compound 62 (0.5 g) was treated with dry acetone and anhyd. cooper sulfate as described for 38. The product was a complex mix ture (Tlc).

O-Benzylation[36] of 62

0.4 g NaH (50% dispersion in mineral oil) was washed with pet ether (5 ml x 3) to remove oil. DMSO (3 ml) was added and stirred for 5 min. in N_2 atmosphere. To this was added 62 (0.250 g) in DMSO (2 ml) dropwise at 25° and stirring continued for 1 hr. Benzylchloride (1.5 g) was added dropwise and stirred for 4-5 hr. Reaction mixture was diluted with ice cold water (10 ml) and extracted with ether (10 x 3), washed, dried and evaporated under reduced pressure. The product was found to be a complex mixture (Tlc.)

O-Diethylidene-D-lyxosediethyldithioacetal; 63

To a stirred soln of 62 (1 g) in paraldehyde (2 ml) at 10-15° was added conc. H_2SO_4 (98%, 0.5 ml) and stirred for 3 hr, diluted with water (10 ml), extracted with pet ether (10 ml x 3), washed with water (5 ml x 3), brine and dried. The solvent was evaporated under reduced pressure to furnish 63 as viscous liquid (0.6 g, 50%). R_f 0.62, 0.42 (Tlc, ether; pet ether; 1:1). $[\alpha]_D$ -45° (c, 0.5%, $CHCl_3$).

IR (Fig. 44) (Neat): 2980, 2940, 1450, 1415, 1380, 1330, 1265, 1150, 1120, 940 and 900 cm^{-1}.

NMR (Fig. 45): $-CH_3$ (12H, m, 1.3 ppm), $S-CH_2$ (4H, m, 2.68 ppm), S-CH, O-CH, $O-CH_2$ (6H, m, 4.0 ppm); $\begin{matrix}O\\O\end{matrix}\!\!>C-H$ (2H, 2m, 4.72 and 5.00 ppm.

Mass (Fig. 46): m/e 308 (M^+, 66.3%), 247 (31.5%), 203 (66.3%), 159 (19.9%), 135 (100%), 131 (58.4%), 113 (24.7%), 99 (28.4%), 75 (66.3%), and 59 (61.5%).

(Found C, 50.12; H, 7.43, S, 20.45. $C_{13}H_{24}S_2O_4$ requires C, 50.64, H, 7.79, S, 20.77%).

Di-O-ethylidene-aldehydo-D-lyxose

(a) Mercuric chloride and cadmium carbonate method. Compound 63 (0.11 g) was treated with mercuric chloride (0.6 g) and cadmium carbonate (0.6 g) in aq. acetonitrile as described for 39. The product obtained was very complex and the required aldehyde was not present in the mixture (PMR).

(b) Using thallium nitrate[38]

To a stirred soln of 63 (0.1 g) in methanol (8 ml) at 25° was added thallium nitrate (0.238 g) soln in methanol (2 ml) and the mixture was stirred for 0.5 hr, filtered, filtrate evaporated. Residue was diluted with water (10 ml) and extracted with chloroform (10 ml x 3), washed, dried and solvent evaporated under reduced pressure. The resulting product was a mixture of compounds (Tlc) and the required aldehyde was not present (PMR).

(c) Methyliodide and acetone[39]. Solution of 63 (0.1 g) in acetone (10 ml containing 1 ml water) and methyliodide (1 ml) was refluxed for 48 hr. Monitoring by Tlc indicated that, there were no reaction. The starting material was recovered, after evaporation of the solvent.

(d) Iodine-DMSO.[40] Solution of thioacetal (0.1 g) and iodine (0.14 g) in DMSO (10 ml) was heated on a steam bath for 1 hr, diluted with water (20 ml), extracted with chloroform (10 ml x 3), washed with aq. sodium thiosulfate (10%, 5 ml x 2), washed with water (5 ml x 3), dried, evaporated. The resulting product contains unchanged starting material.

D-lyxose diethyldithioacetal tetraacetate; 65

A soln of 62 (1 g) in acetic anhydride (8 ml) and dry pyridine (6 ml) was stirred at 25° for 16 hr, diluted with water (20 ml), extracted with ether (20 ml x 3). The extract was washed with ice cold aq. hydrochloric acid (5%, 10 ml x 2), washed with water, dried. Solvent removal furnished 65 (1.2 g, 70%), m.p. 37-38° (lit.[43], m.p. 38.5°). $[\alpha]_D$ + 50 (c, 0.45%, MeOH), lit. [43], $[\alpha]_D$ + 50.3 (c, 0.31%, MeOH).
R_f 0.45 (Tlc, 50% EtOAc in benzene).
PMR: C-C$\underline{H}_3$ (6H, t, 1.85 ppm, J = 8Hz); -$\overset{O}{\overset{\|}{C}}$-C$\underline{H}_3$ (12H, 3s, 2.03, 2.09, 2.12 ppm); -S-C$\underline{H}_2$ (4H, m, 2.65 ppm); O-C-$\underline{H}$, O-C-$\underline{H}$ (2H, m. 3.78 ppm); O-C-$\underline{H}$ (1H, m. 4.24 ppm); O-C$\underline{H}$ (2H, m. 5.29 ppm); O-C$\underline{H}$ (1H, dd, 5.6 ppm); J_1 = 8Hz, J_2 = 2Hz).

Aldehydo-D-lyxosetetraacetate[42] 66

To a stirred soln of 65 (0.2 g) in aq. acetic acid (70%, 4 ml) at 25°, was added dropwise a soln of bromine (0.15 g) in aq. acetic acid (80%, 1 ml), followed by sodium acetate (0.4 g) and stirred for 0.5 hr. Diluted with saturated aq. sodium bicarbonate soln (30 ml) at 0-10°, extracted with pet ether (10 ml x 2) to remove sulfide by-products. And then extracted with chloroform (10 ml x 3). Chloroform extract was washed with water (10 ml x 3), brine and dried. Solvent removal furnished viscous liquid, 66 (0.12 g, 80%).

$[\alpha]_D$ - 40 (c, 0.5%, $CHCl_3$).

PMR: O-C-CH_3 (12H, 4s, 2.08, 2.1, 2.13 and 2.2 ppm); O-CH_2 O-CH (3H, m, 4.12 ppm); O-CH (2H, m, 5.32 ppm) C(=O)-H (1H, s, 9.49 ppm).

Wittig reaction of 66

Compound 66 (0.1 g) was subjected to Wittig reaction with triphenyltridecylphosphorane as described for 40. The required olefin was not present in the reaction product (PMR).

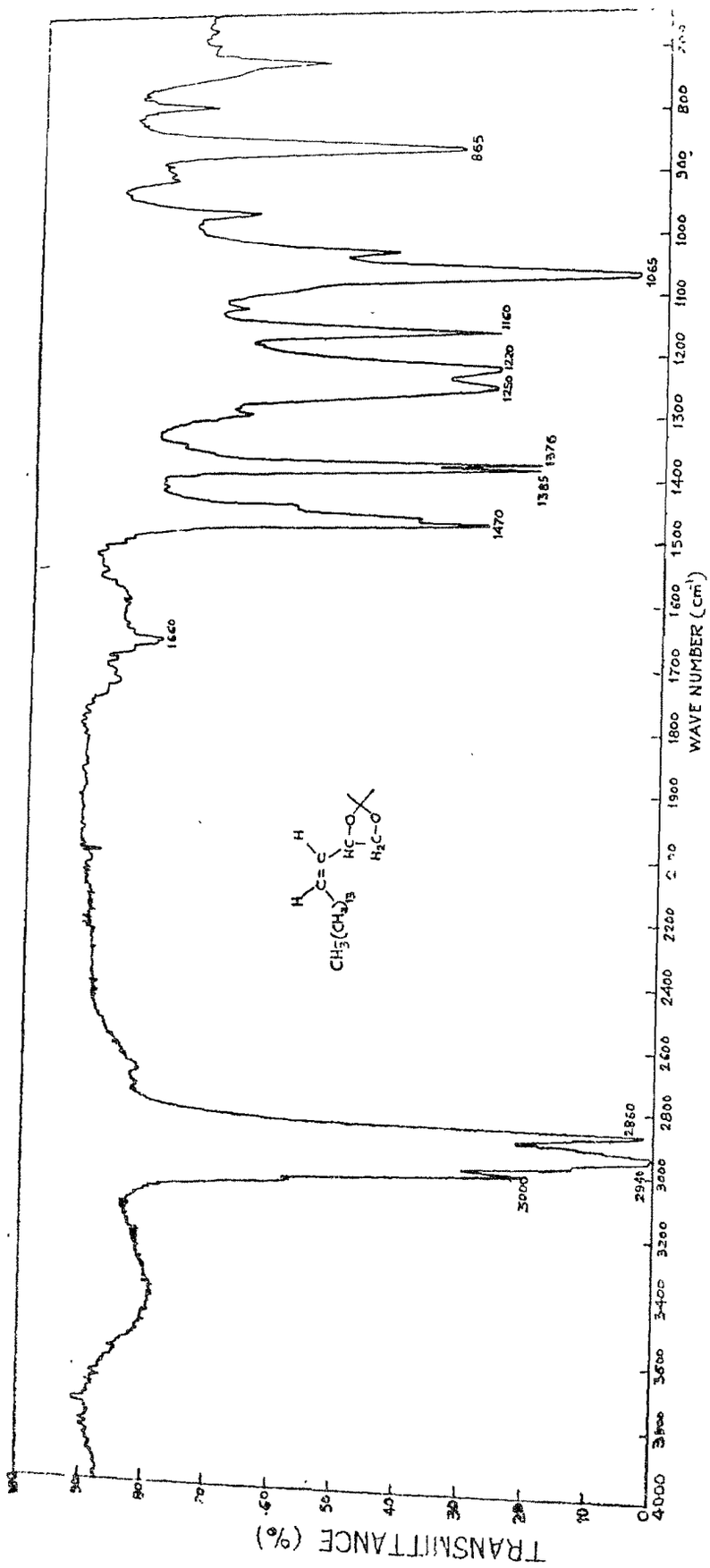


Fig. 13 - IR SPECTRUM OF 1,2,-O-ISOPROPYLIDENE-cis-1,2-OCTADEC E-3-NEDIOL (24)

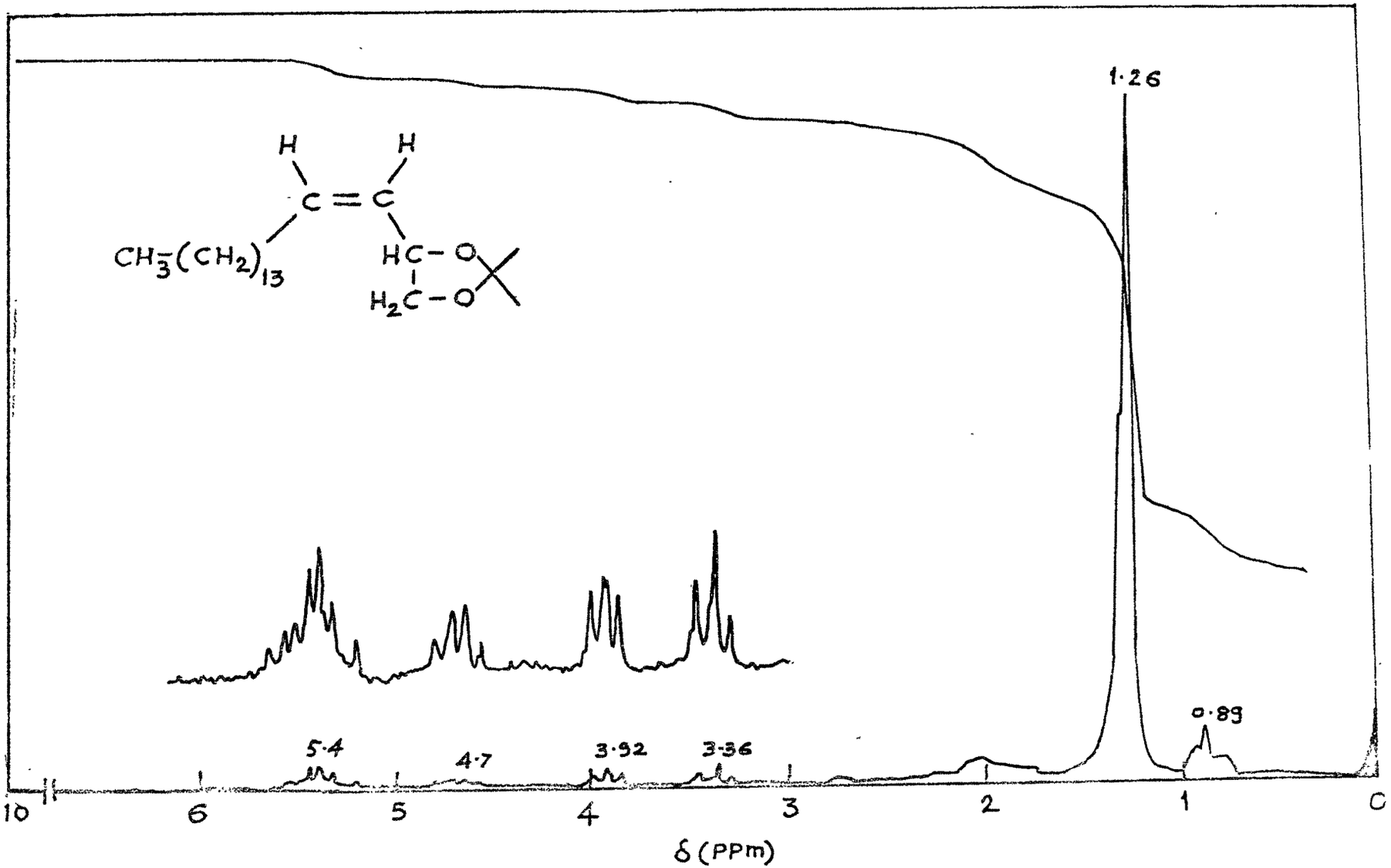


Fig. 14. PMR SPECTRUM OF 1,2-O-ISOPROPYLIDENE-cis-1,2-OCTADEC-3-ENEDIOL (24)

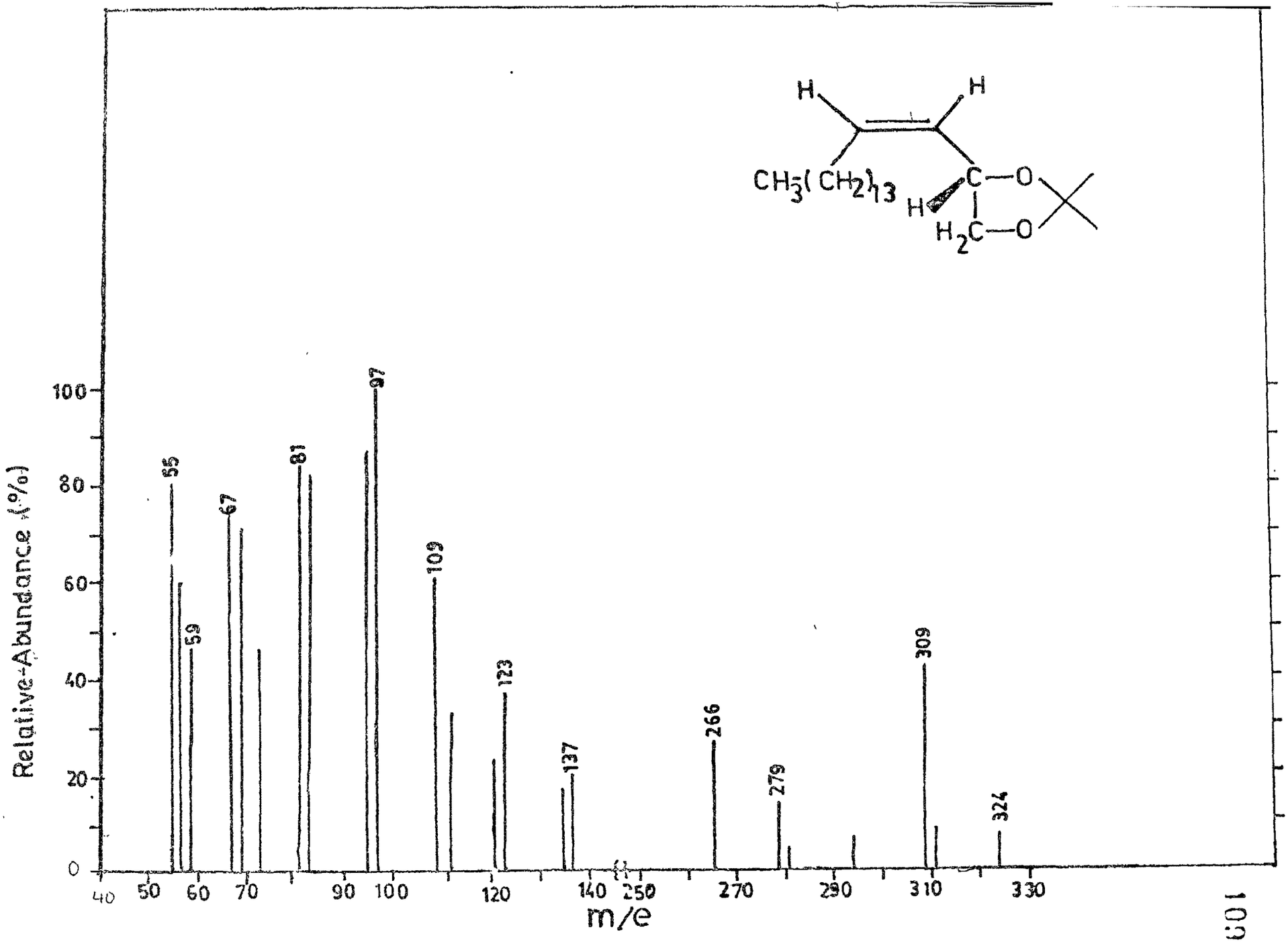


Fig. 15. Mass Spectrum of 1,2-O-isopropylidene-cis-1,2-octadec-3-ene-diol(24)

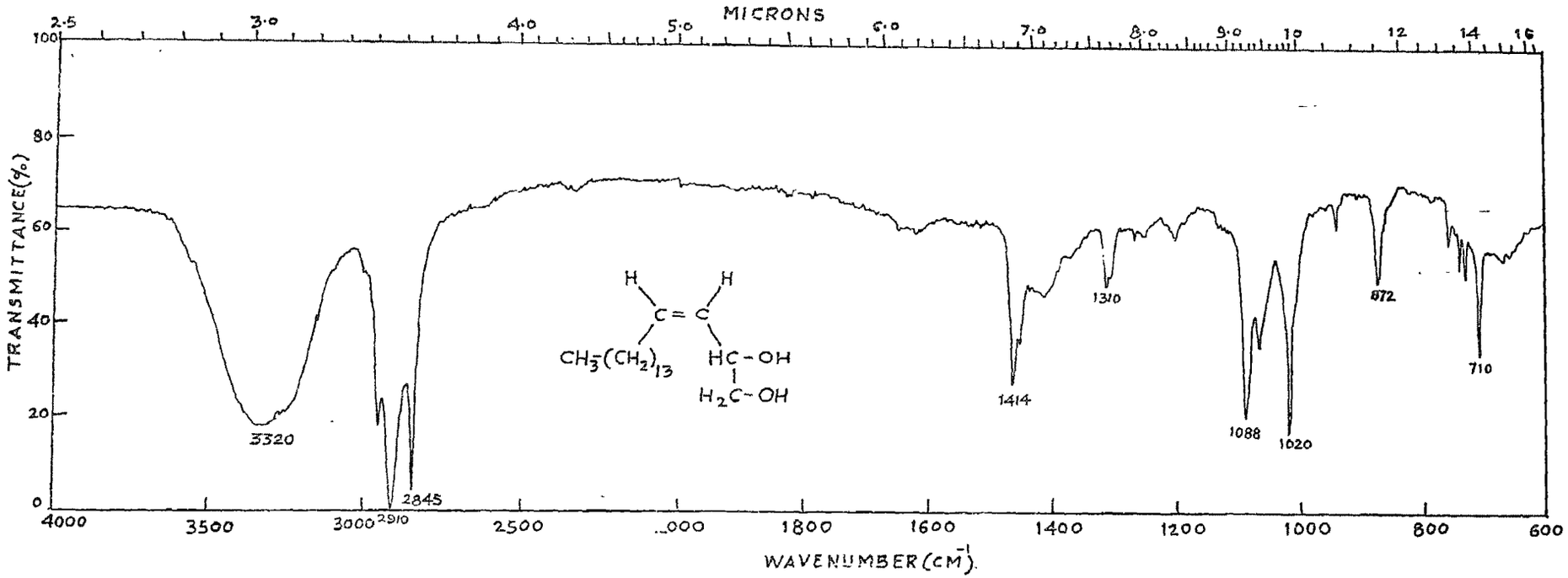


Fig. 16 - IR SPECTRUM OF cis-1,2-OCTADEC-3-ENEDIOL (25)

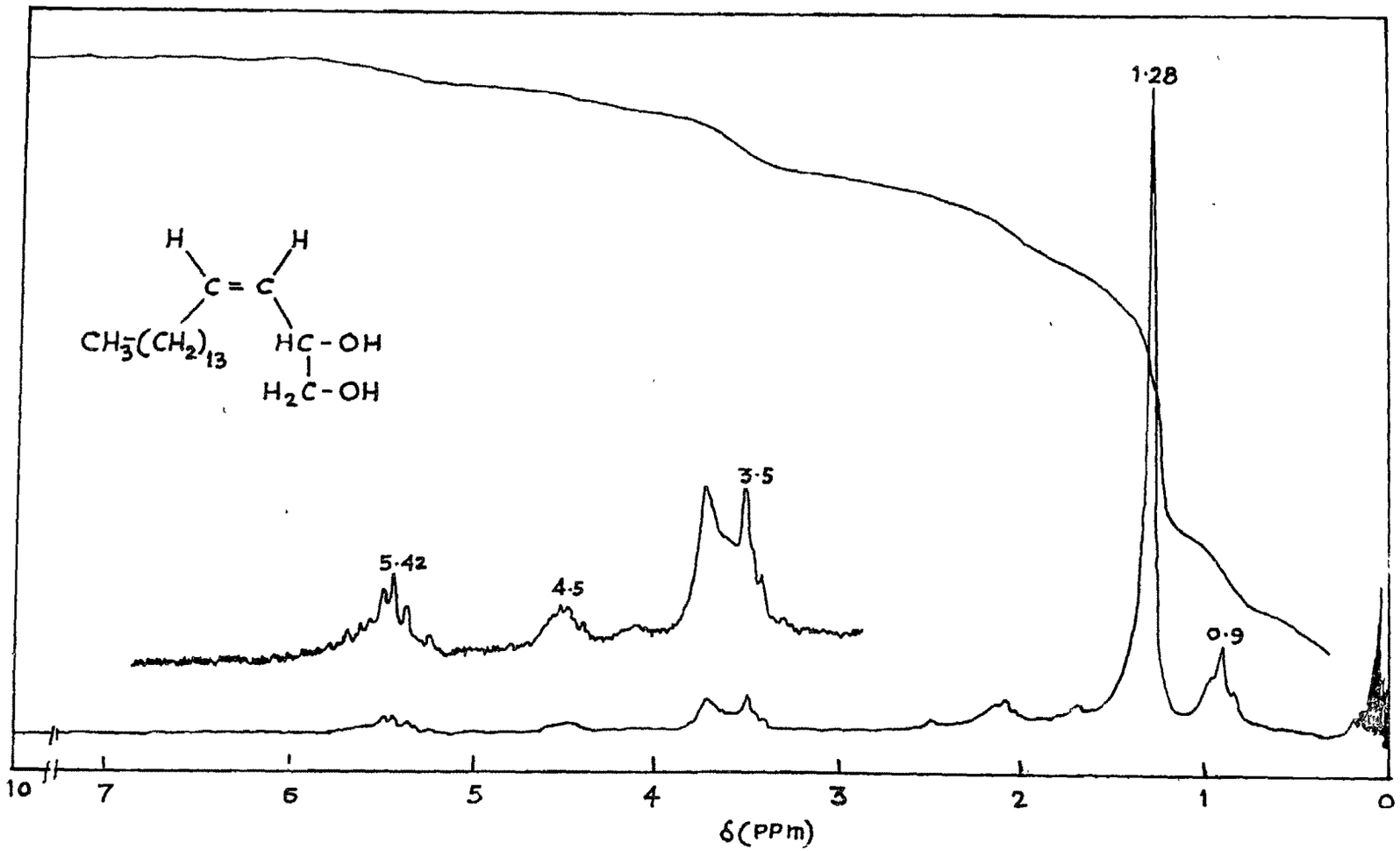


Fig. 17 - PMR SPECTRUM OF cis-1,2-OCTADEC-3-ENEDIOL (25)

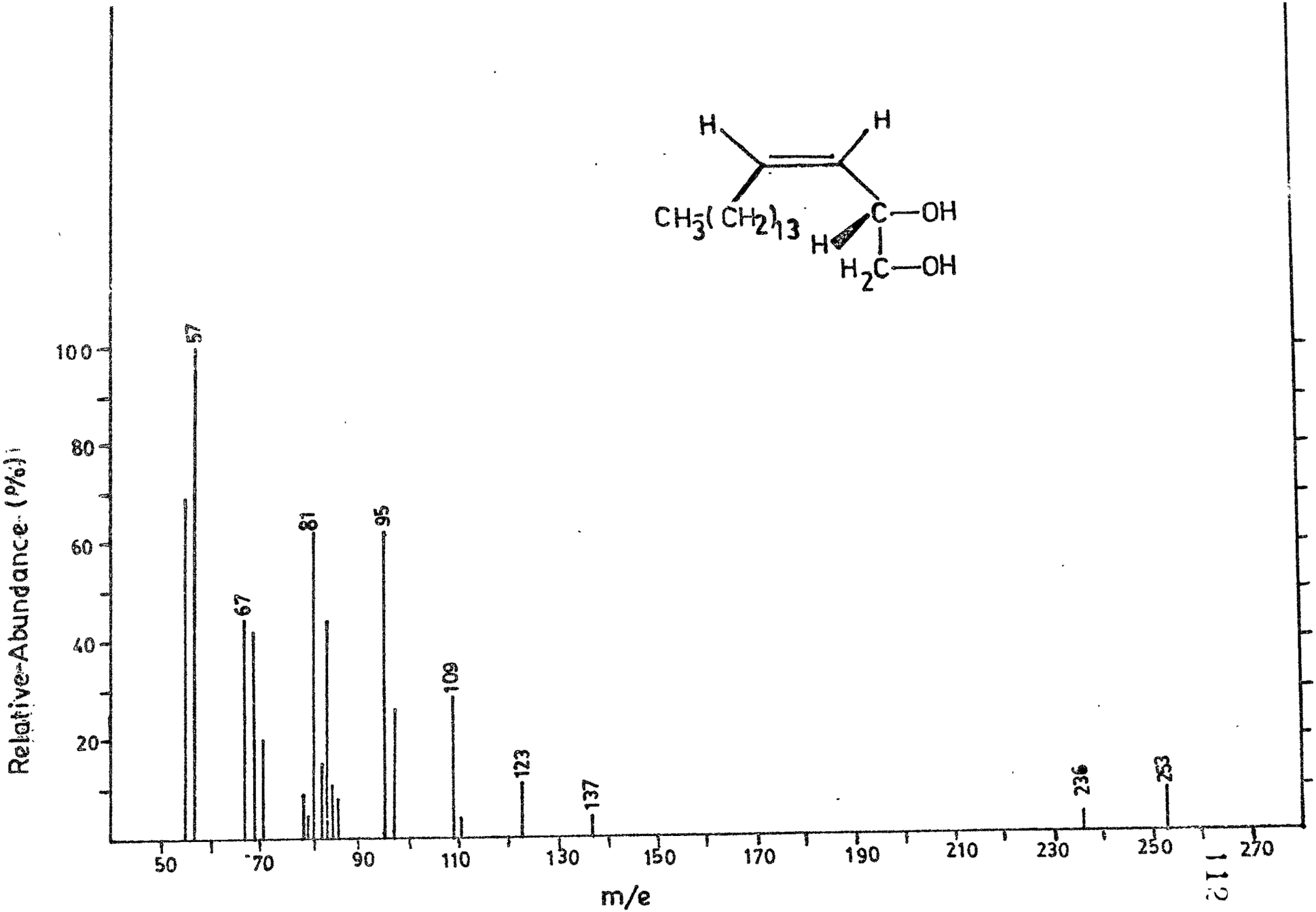


Fig. 18 - MASS SPECTRUM OF cis-1,2-OCTADEC-3-ENEDIOL (25)

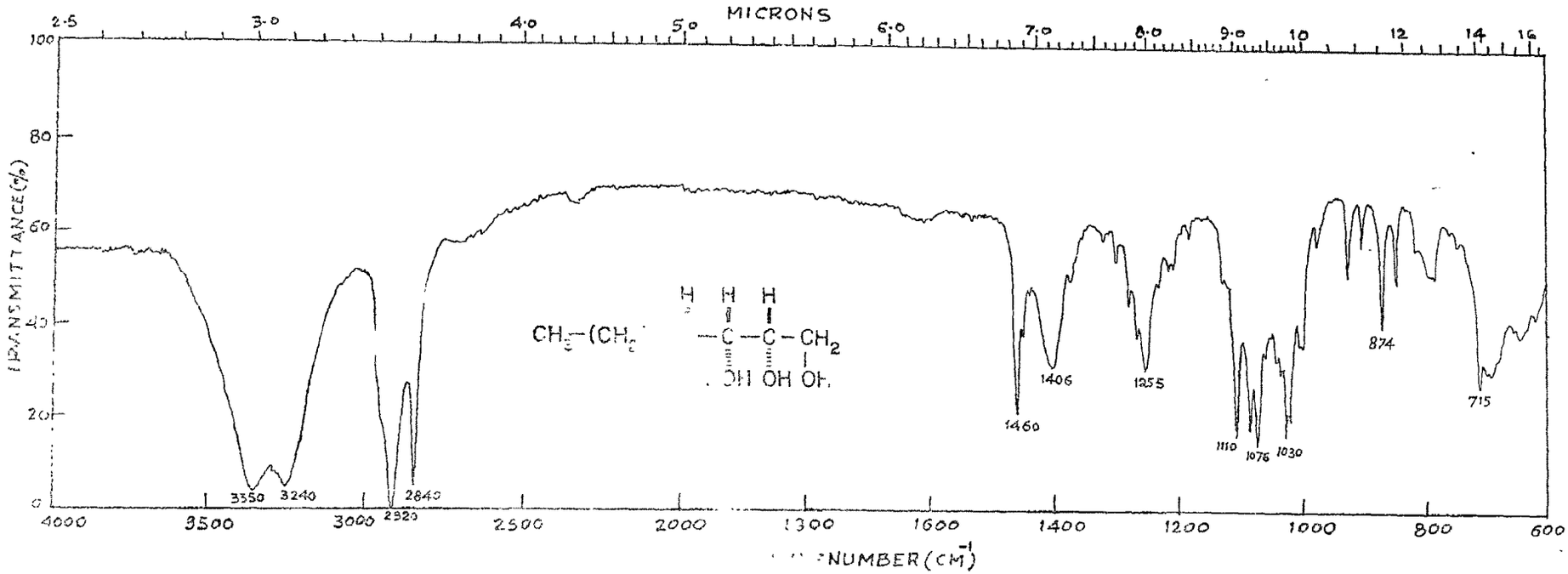


Fig. 19 - IR SPECTRUM OF D-ARABINO-1,2,3,4-OCTADECANETETROL (28)

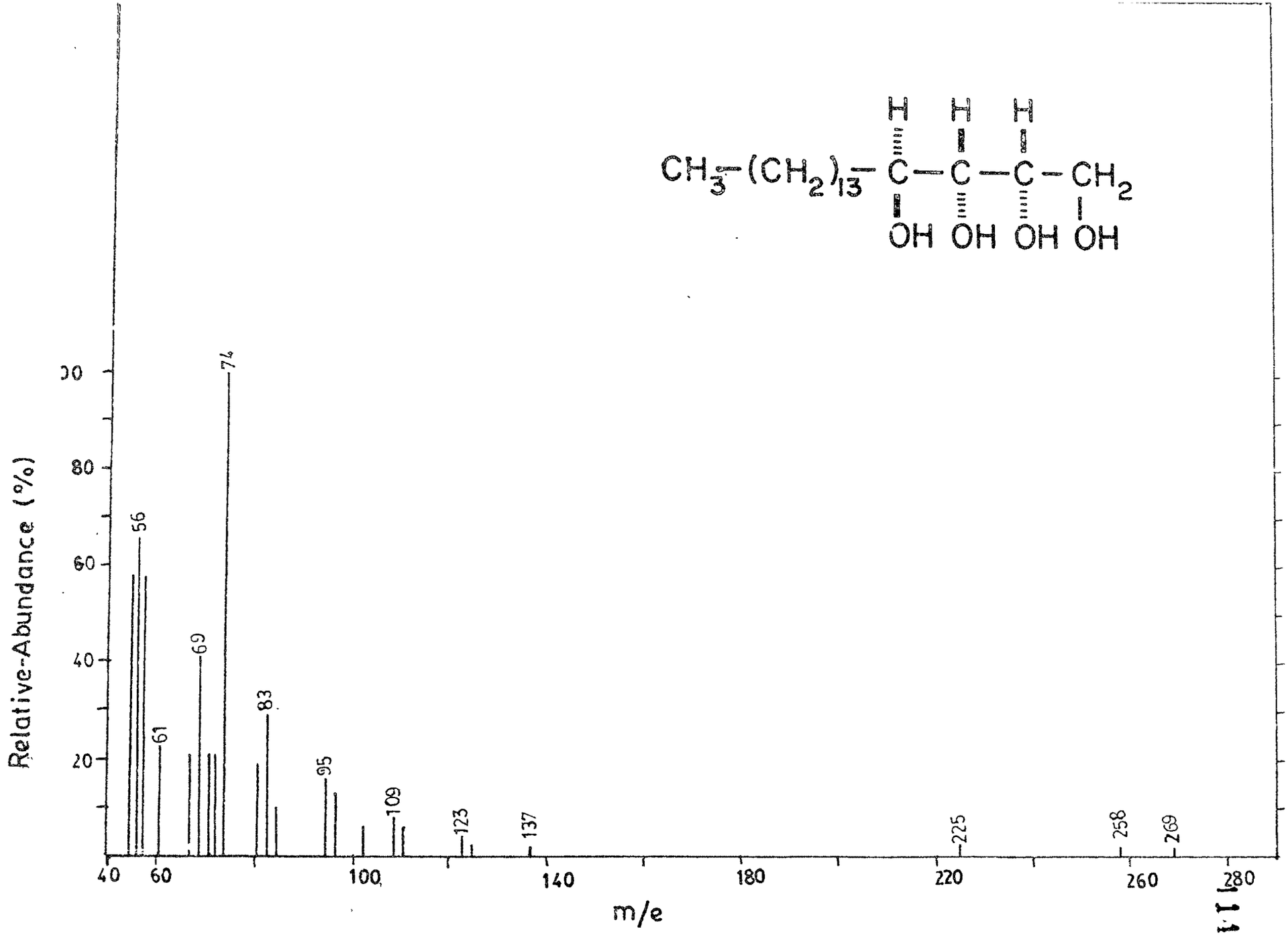


Fig. 20 - MAS SPECTRUM OF D-ARABINO-1,2,3,4-OCTADECANETETROL (28):

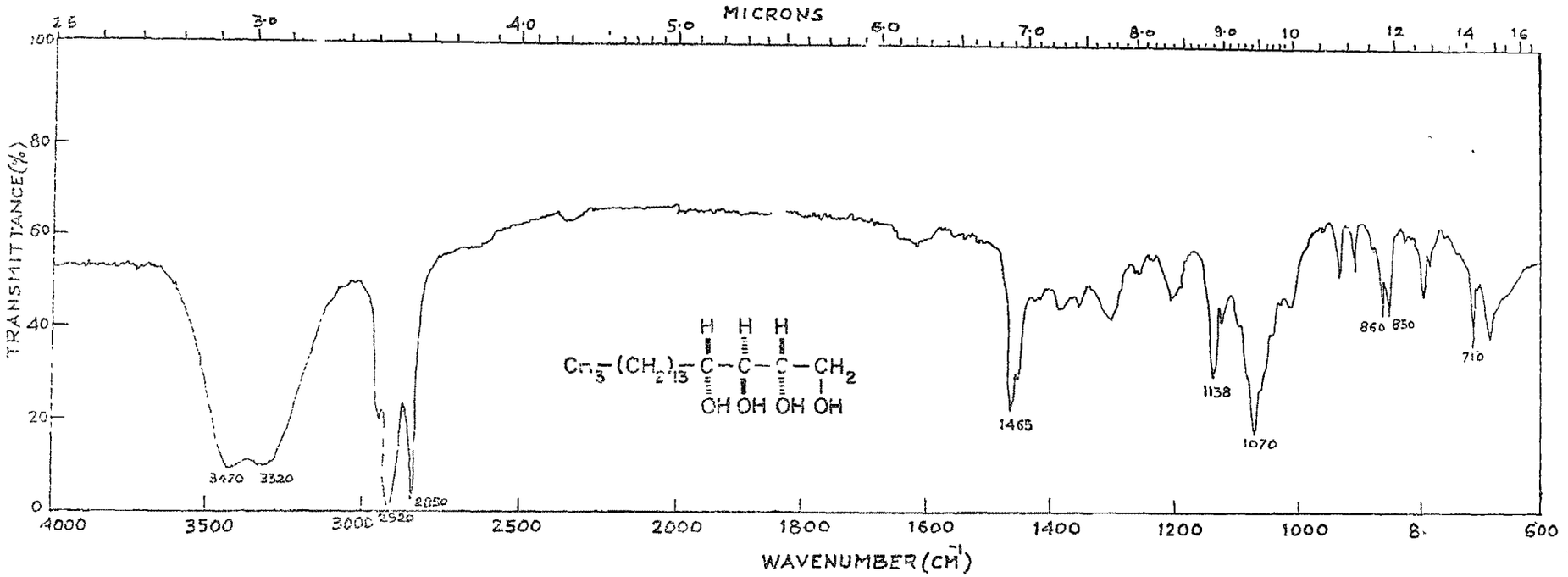


Fig. 21 - IR SPECTRUM OF D-XYLO-1,2,3,4-OCTADECANETETROL (27)

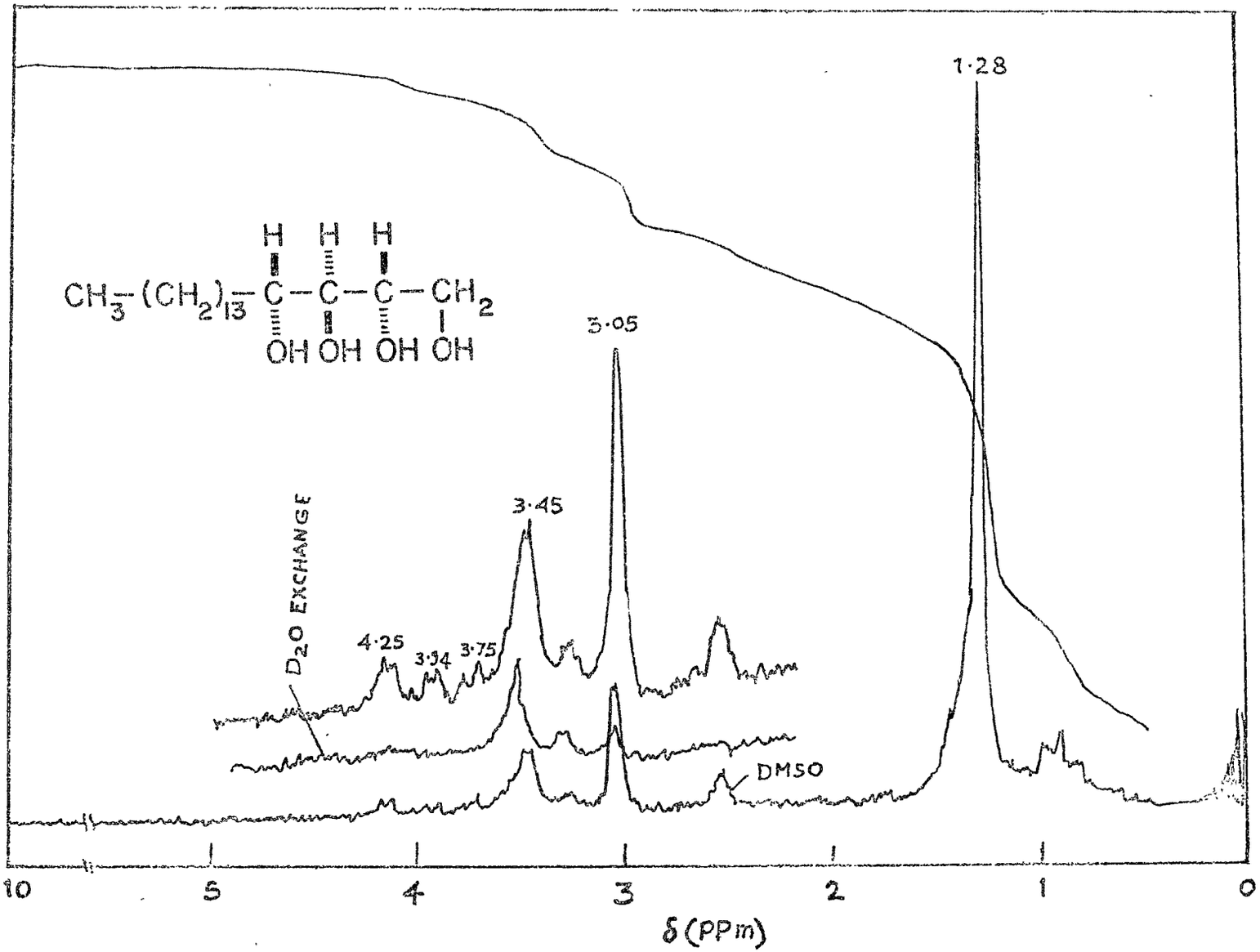


Fig. 22 - PMR SPECTRUM OF D-XYLO-1,2,3,4-OCTADECANETETROL (27)

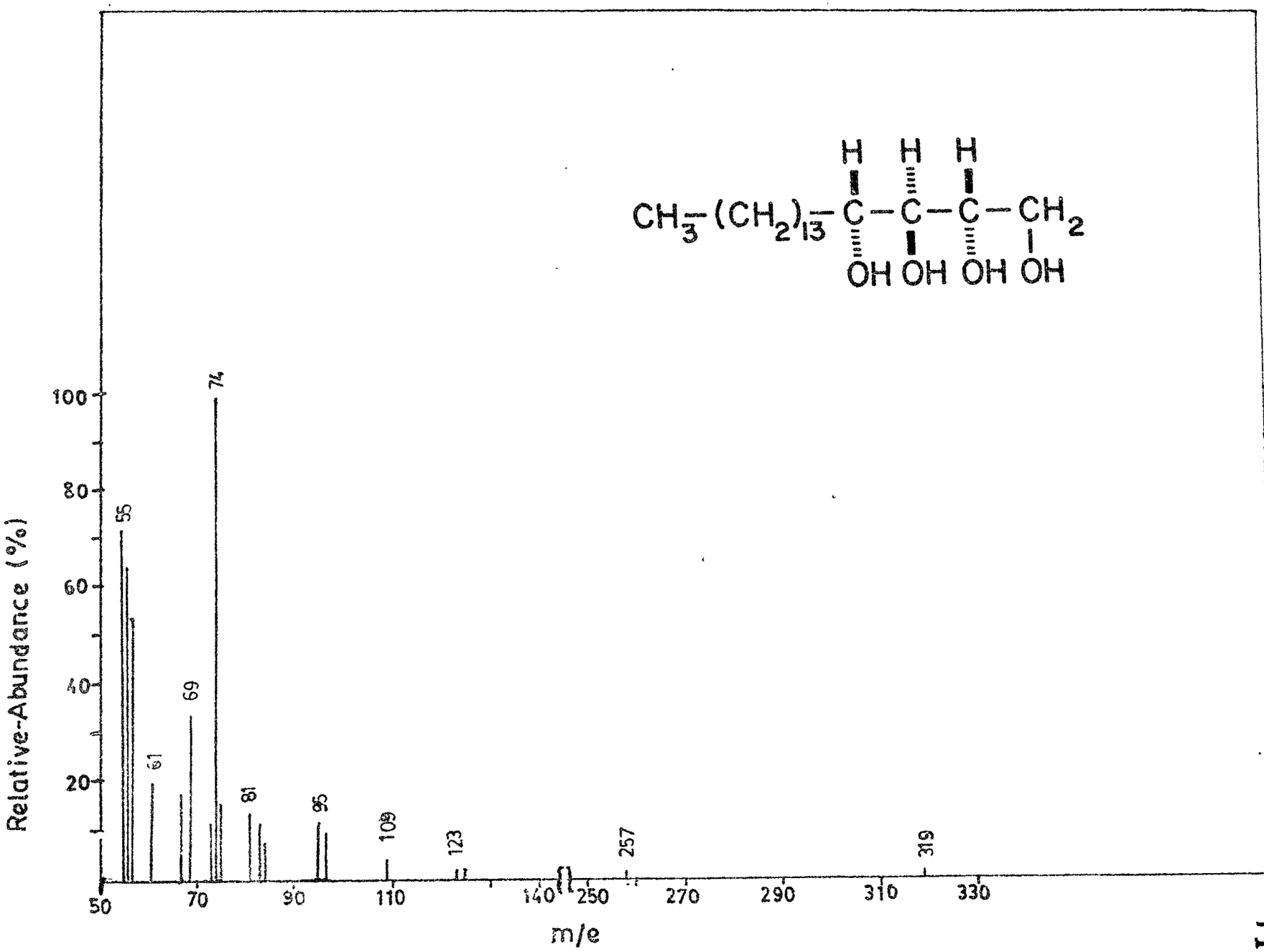


Fig. 23 - MASS SPECTRUM OF D-XYLO-1,2,3,4-OCTADECANETETROL (27)

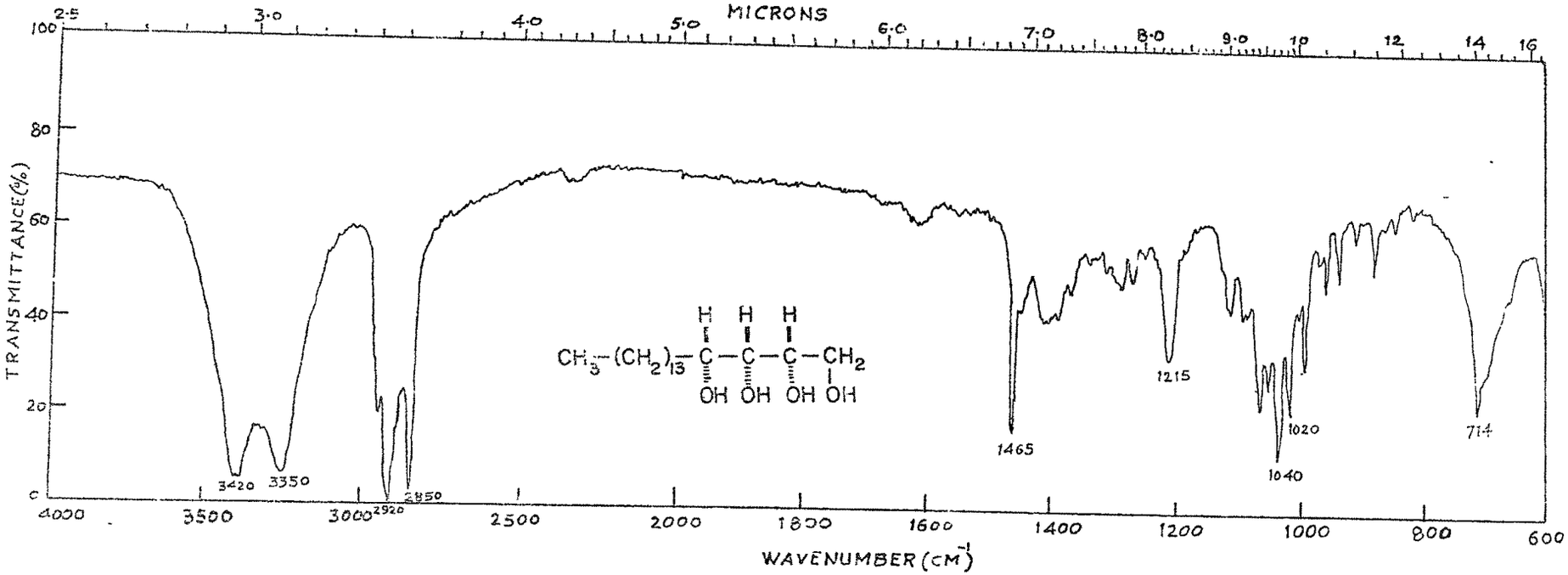


Fig. 24 - IR SPECTRUM OF D-RIBO-1,2,3,4-OCTADECANETETROL (31)

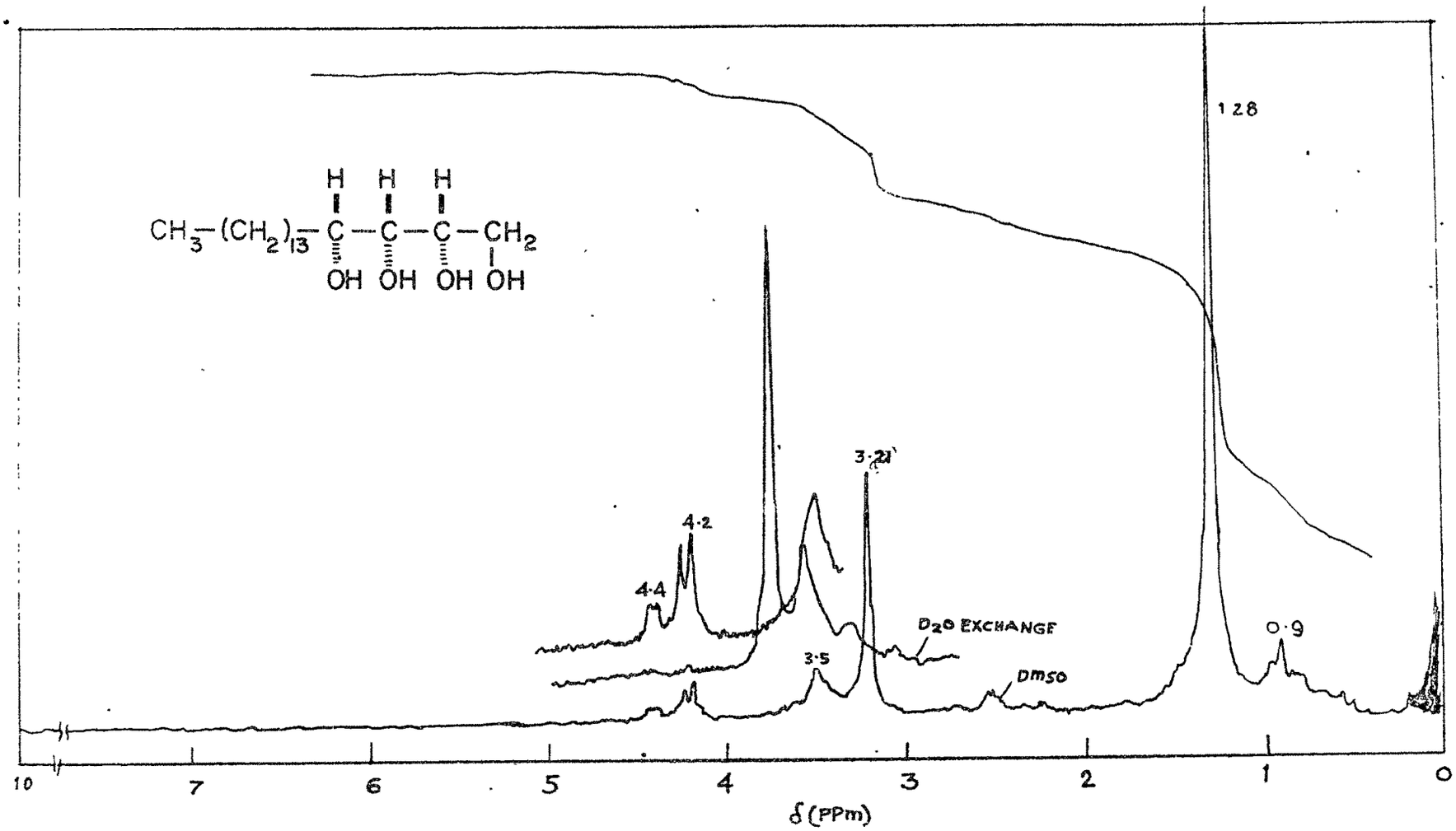


Fig. 25 - PMR SPECTRUM OF D-RIBO-1,2,3,4-OCTADECANETETROL (31)

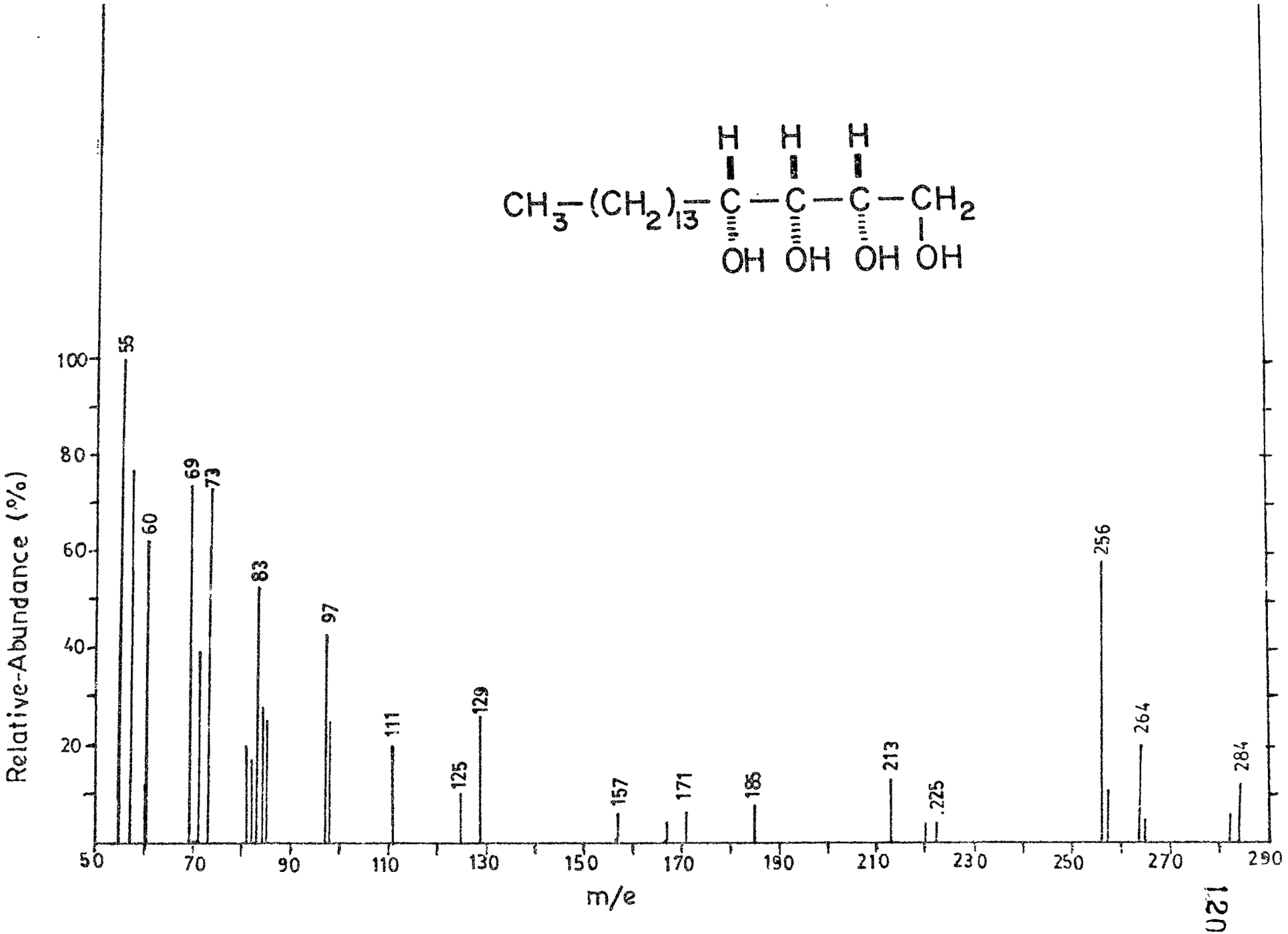


Fig. 26 - MASS SPECTRUM OF D-RIBO-1,2,3,4-OCTADECANETETROL (31)

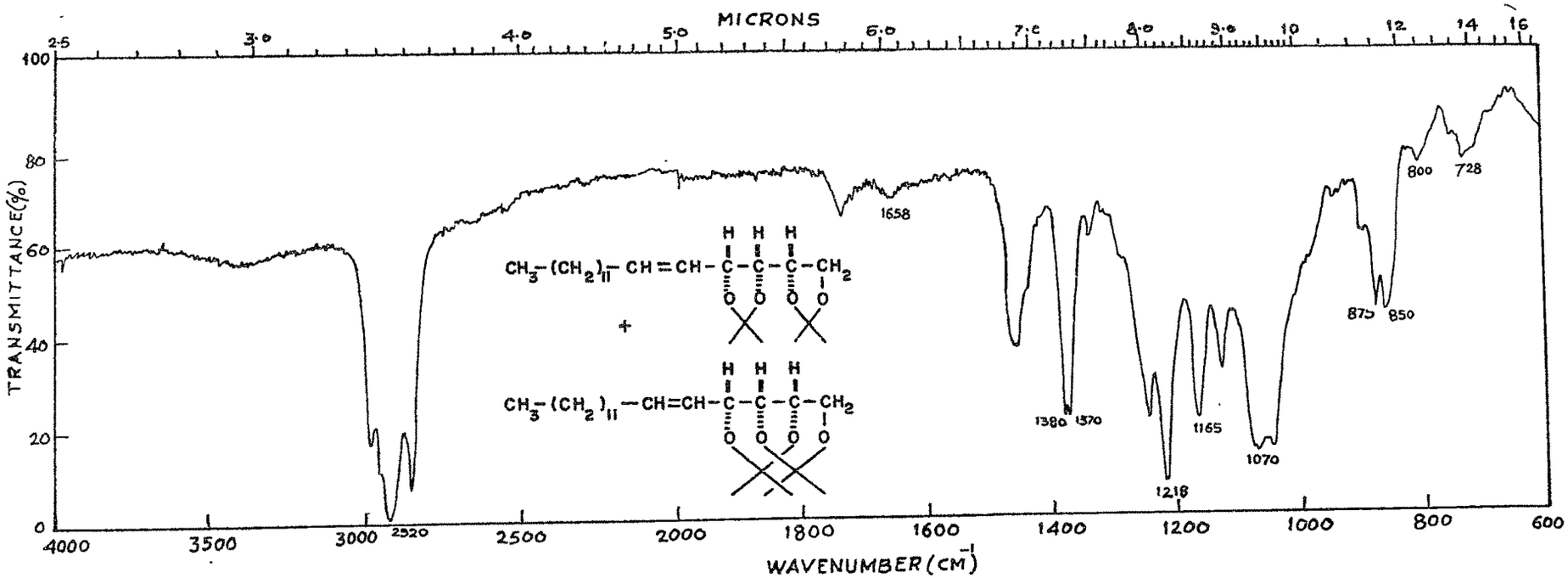


Fig. 27 - IR Spectrum of 1,2;3,4-, and 1,3;2,4-di-O-isopropylidene-D-ribo-1,2,3,4-octadec-5-ene-tetrols (44).

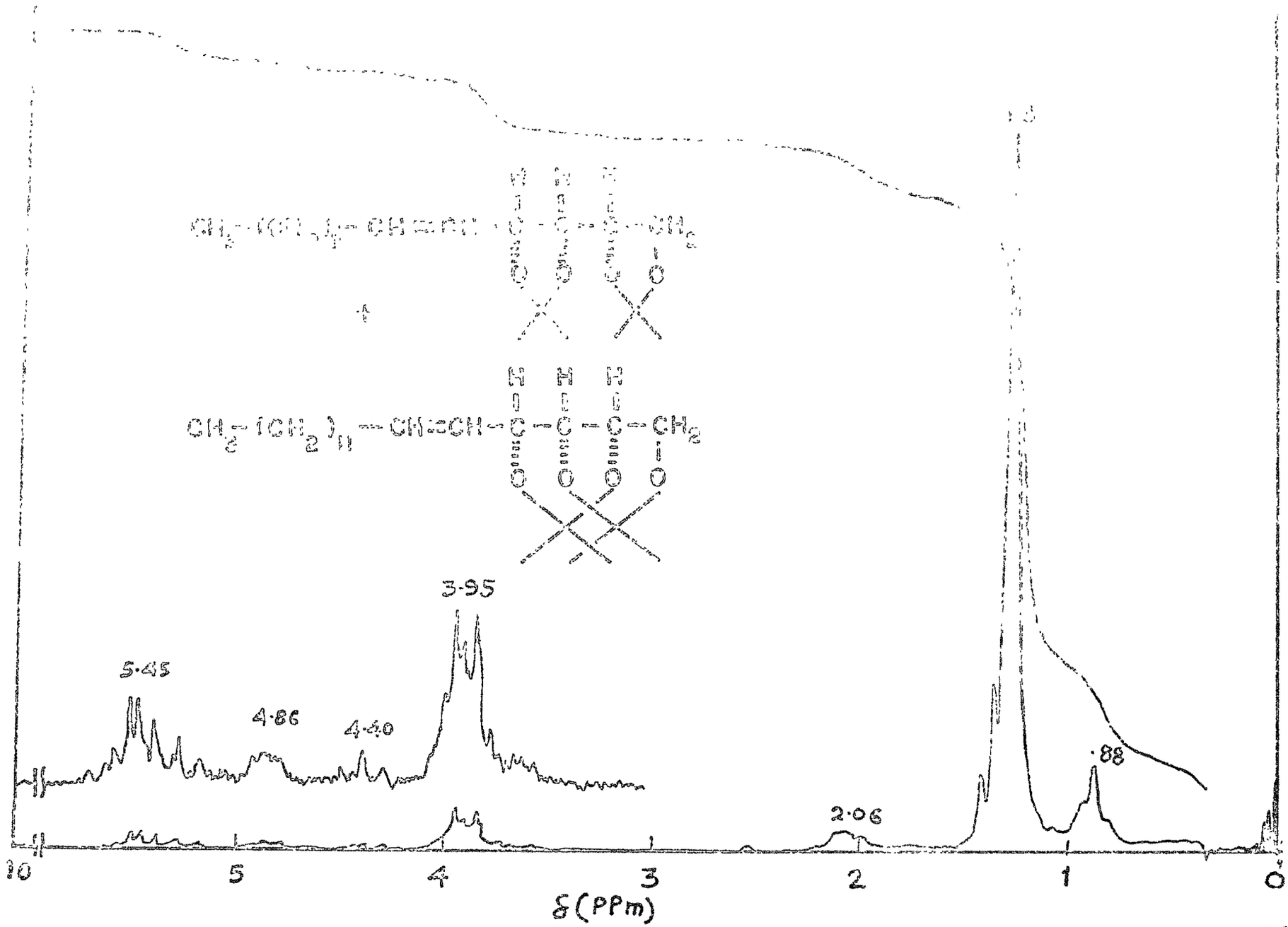


Fig. 28 - PMR Spectrum of 1,2;3,4-, and 1,3;2,4-di-O-isopropylidene-D-ribo-1,2,3,4-octadec-5-ene-tetrol (44)

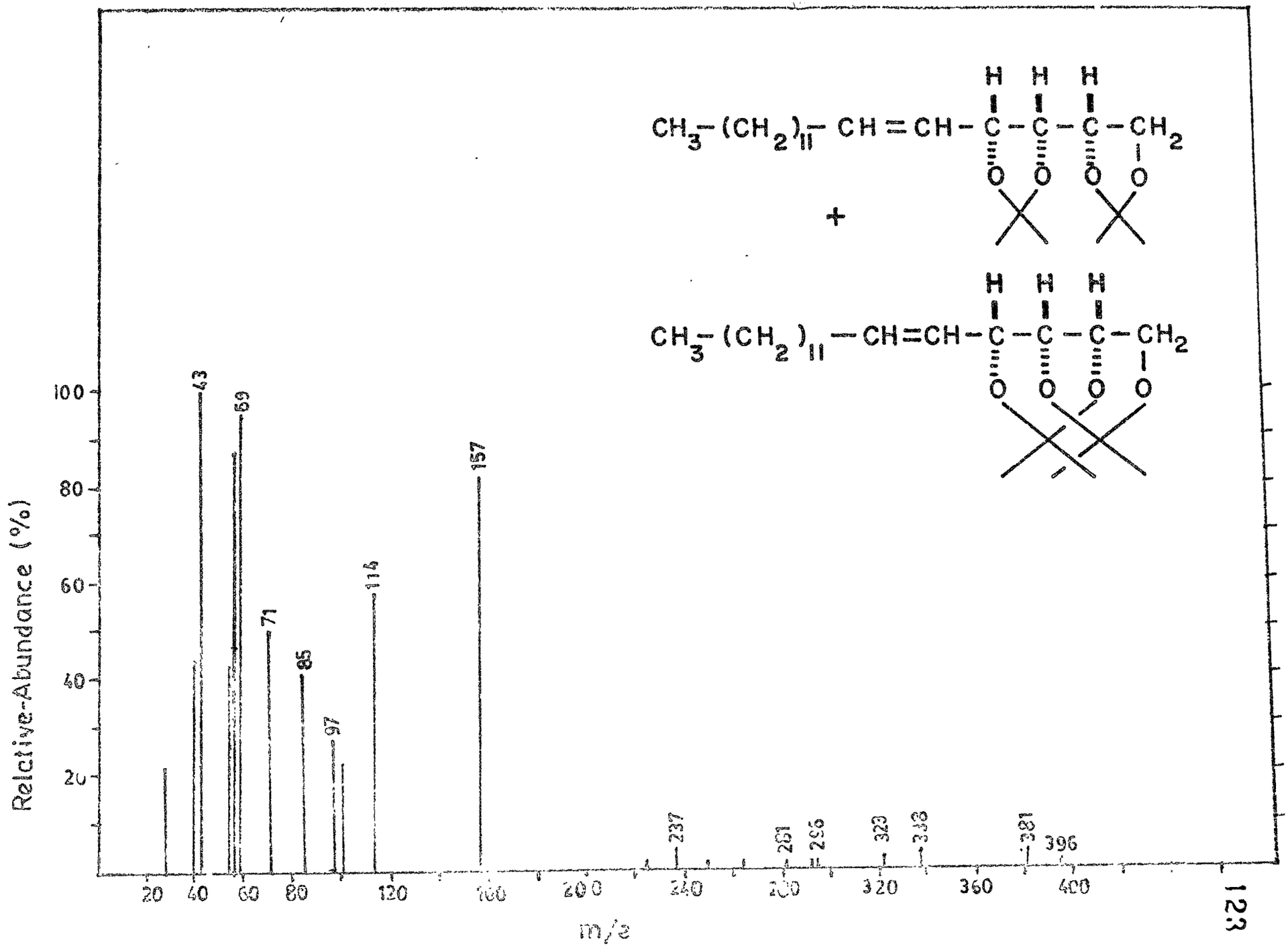


Fig. 29 - Mass spectrum of 1,2;3,4-, and 1,3;2,4-di-O-isopropylidene-D-ribo-1,2,3,4-octadec-5-ene-tetrols (44)

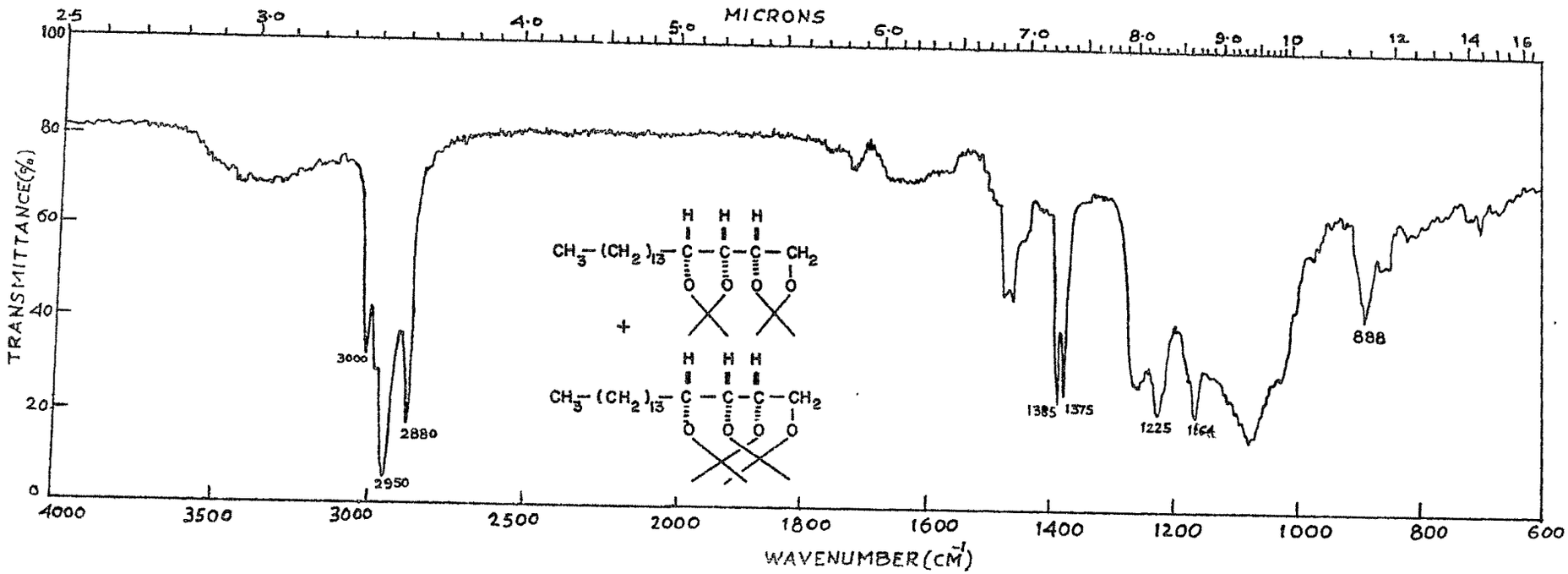


Fig. 30 - IR Spectrum of 1,2;3,4-, and 1,3;2,4-di-O-isopropylidene-D-ribo-1,2,3,4-octadecanetetrols (45)

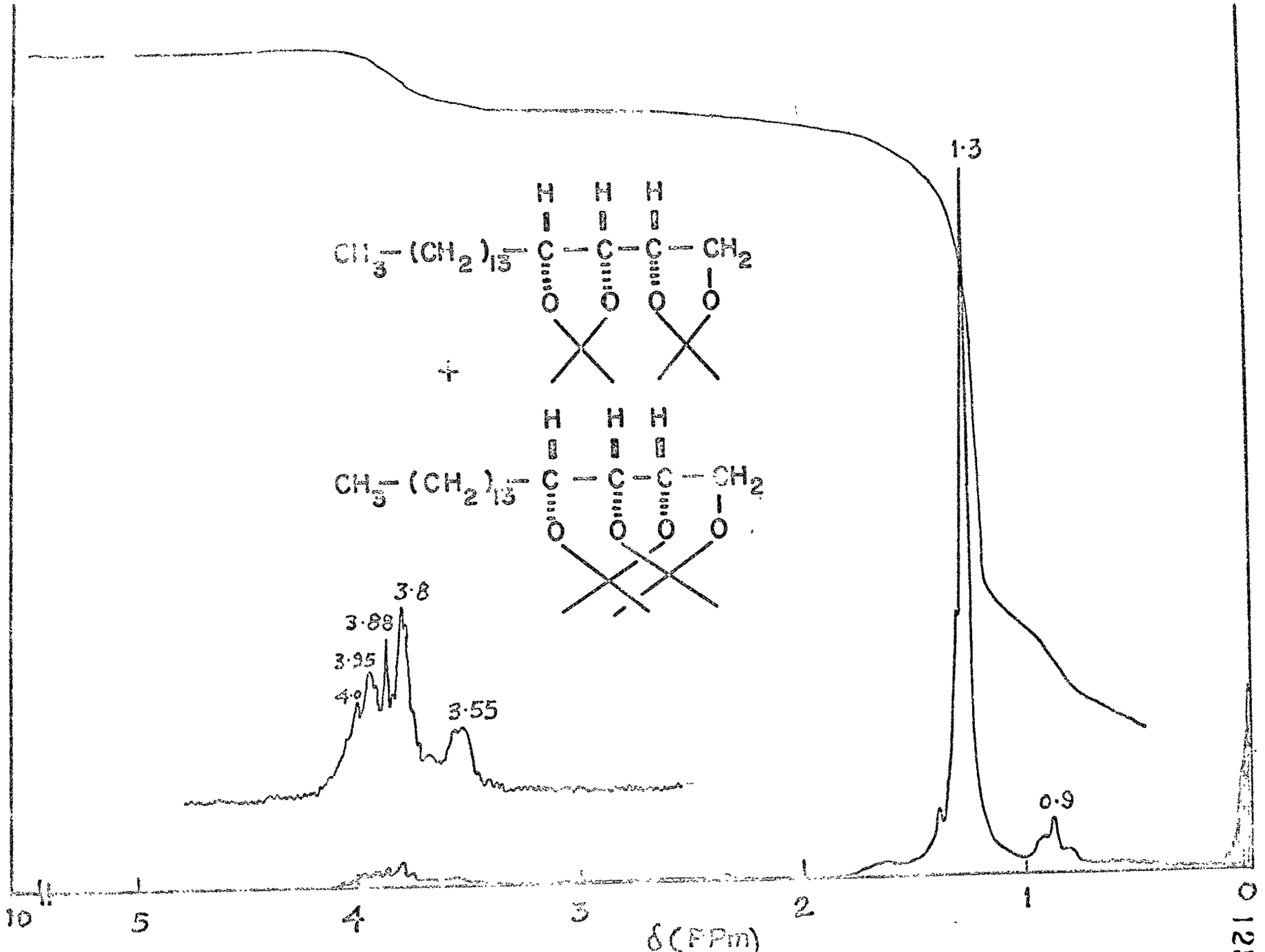


Fig. 31 - PMR Spectrum of 1,2;3,4-, and 1,3;2,4-di-O-isopropylidene-D-ribo-1,2,3,4-octadecanetetrols (45)

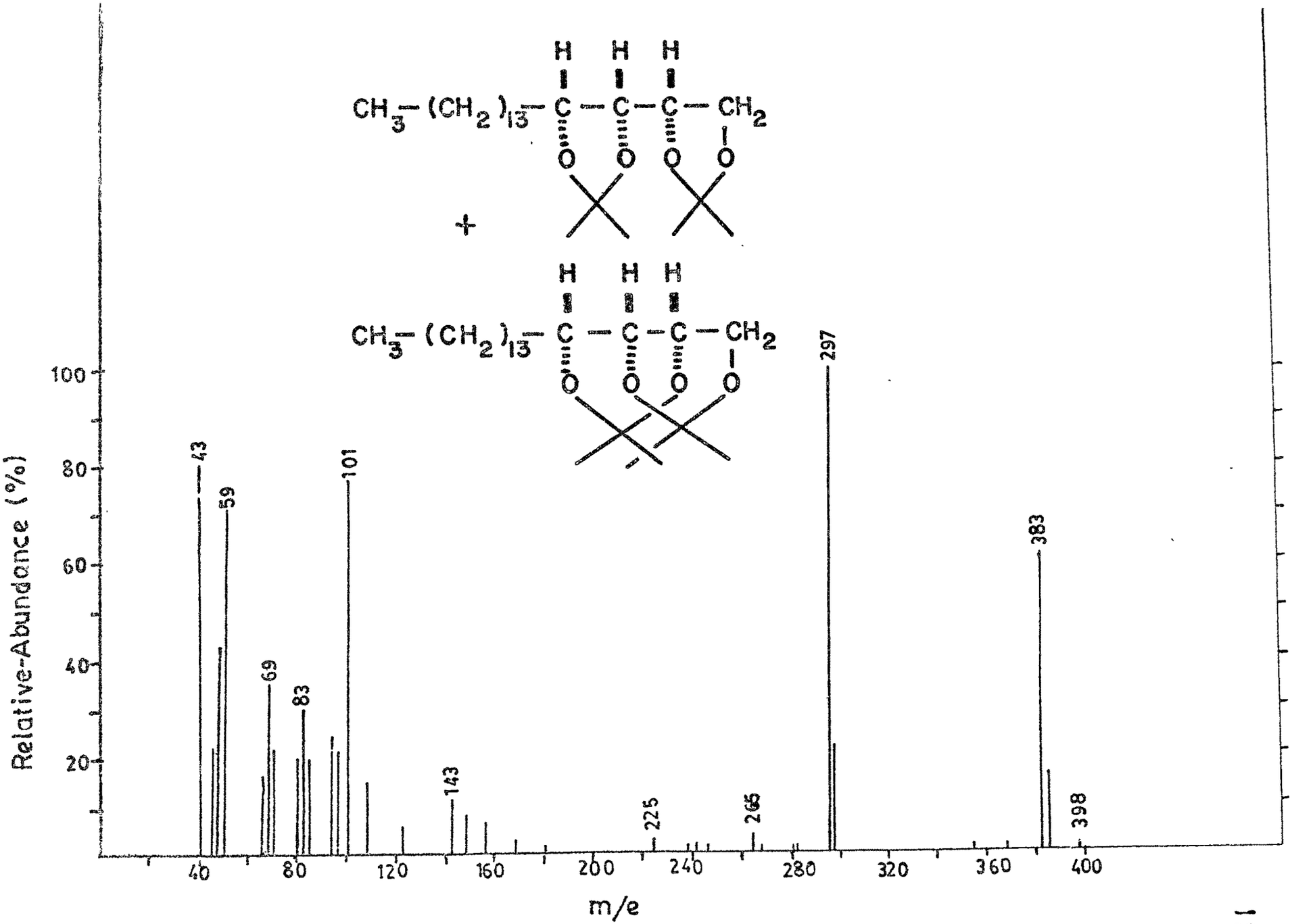


Fig. 32 - Mass spectrum of 1,2;3,4-, and 1,3;2,4-di-O-isopropylidene-D-ribo-1,2,3,4-octadecanetetrols (45)

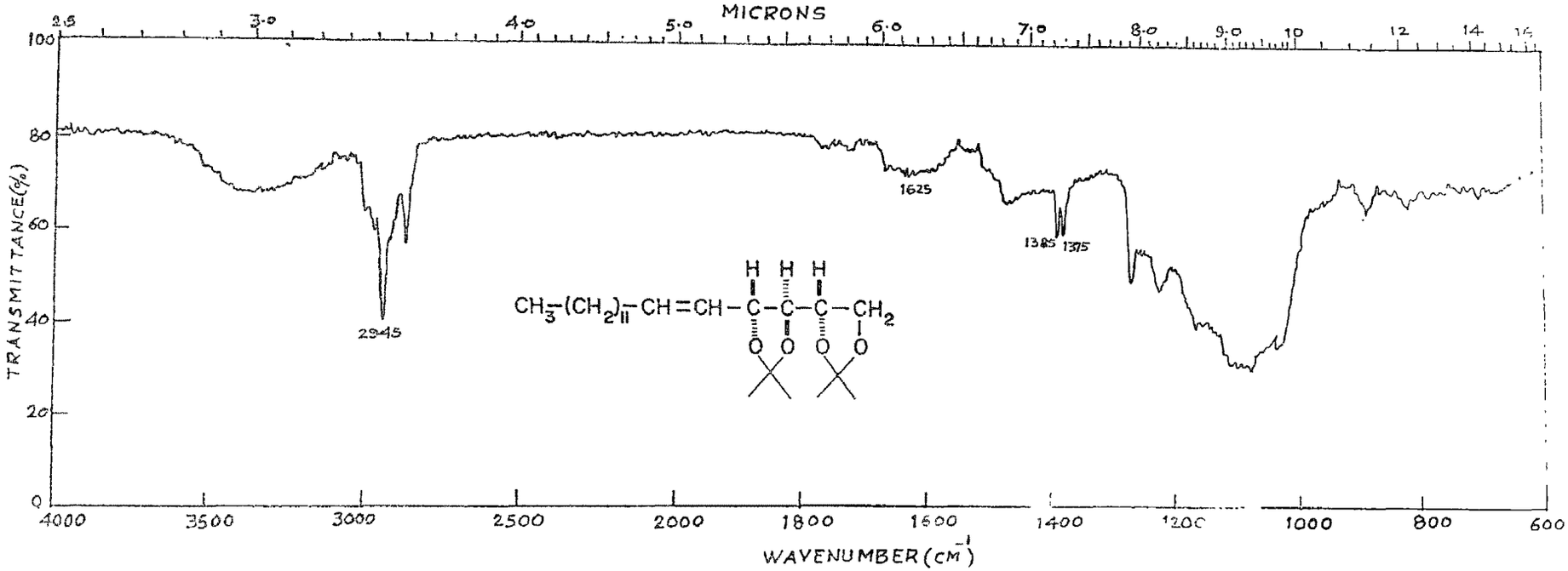


Fig. 33 - IR Spectrum of 1,2;3,4-di-O-isopropylidene-D-xylo-1,2,3,4-octadec-5-ene-tetrol (50)

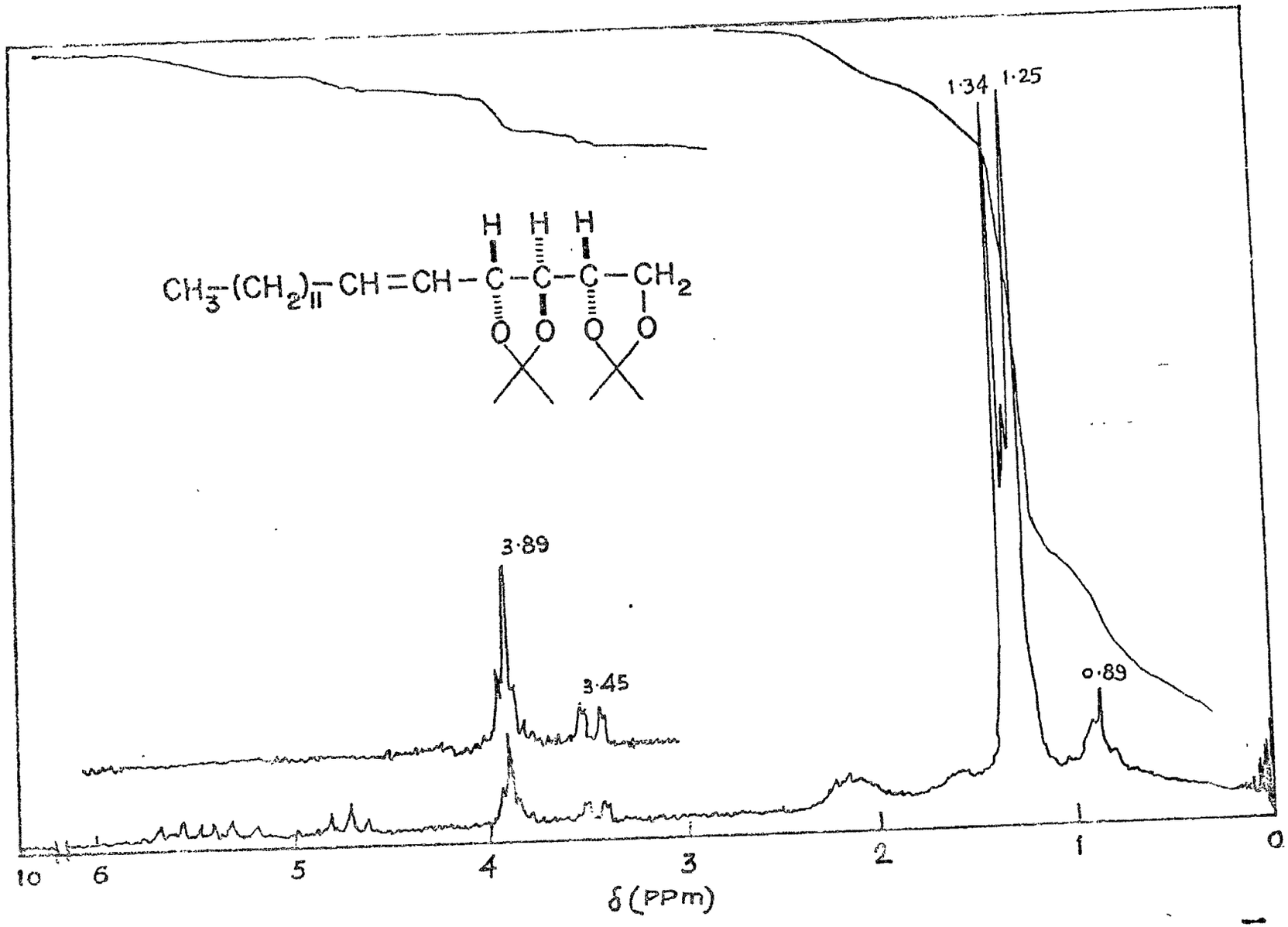


Fig. 34 - PMR Spectrum of 1,2;3,4-di-O-isopropylidene-D-xylo-1,2,3,4-octadec-5-ene-tetrol (50)

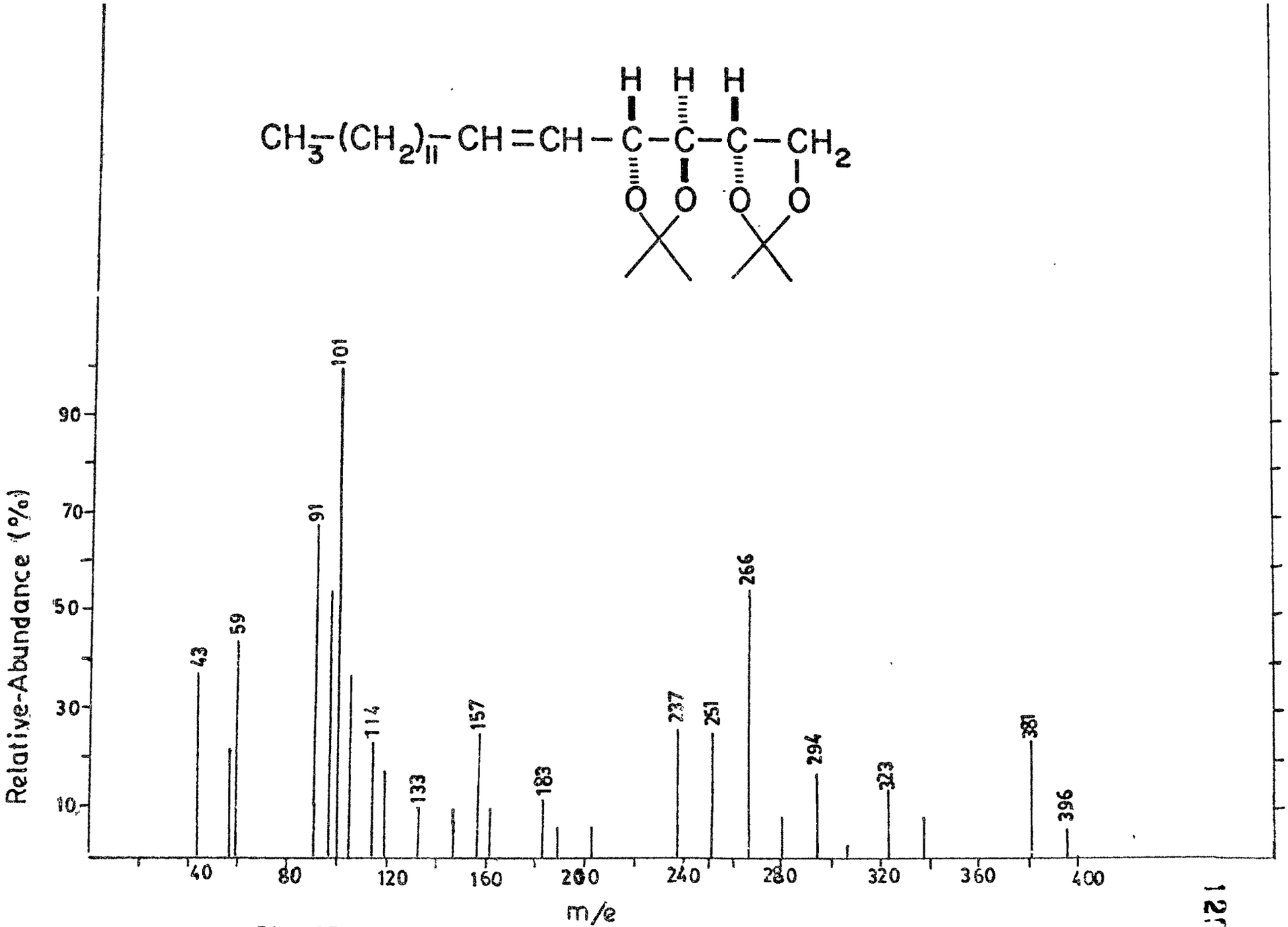


Fig. 35 - Mass Spectrum of 1,2;3,4-di-O-isopropylidene-D-xylo-1,2,3,4-octadecane5-netetrol (50)

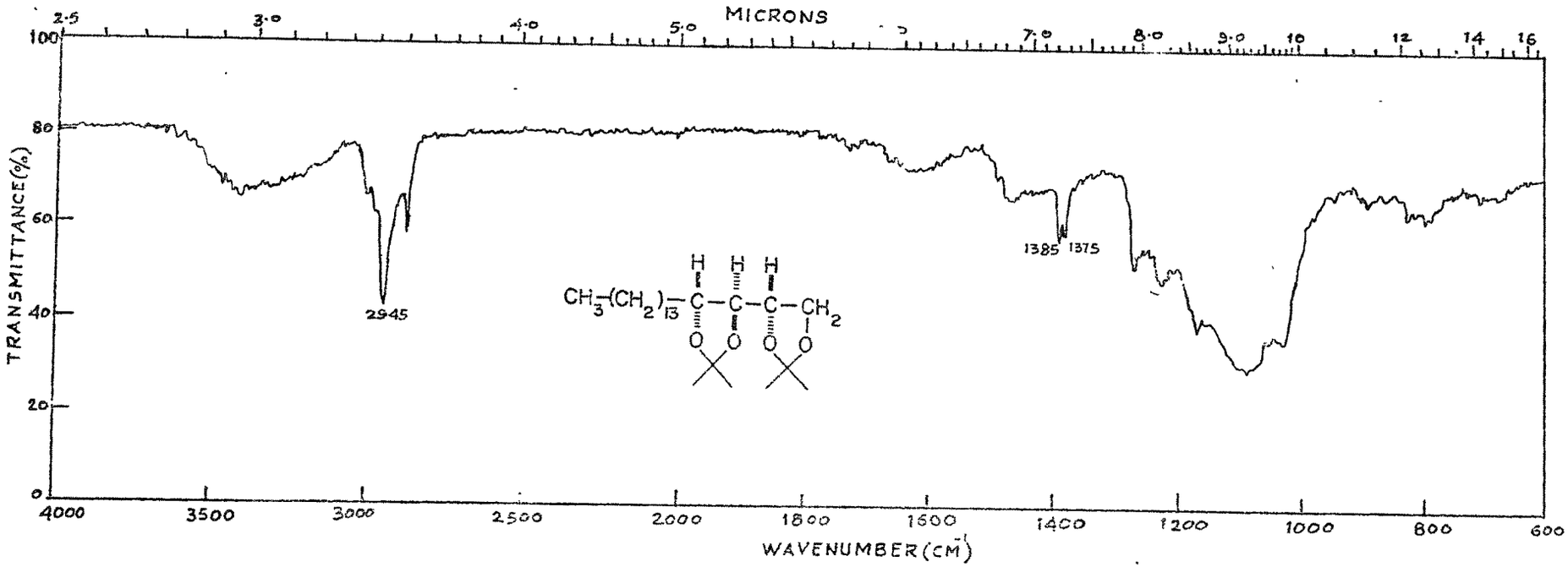


Fig. 36 - IR Spectrum of 1,2;3,4-di-O-isopropylidene-D-xylo-1,2,3,4-octadecanetetrol (51)

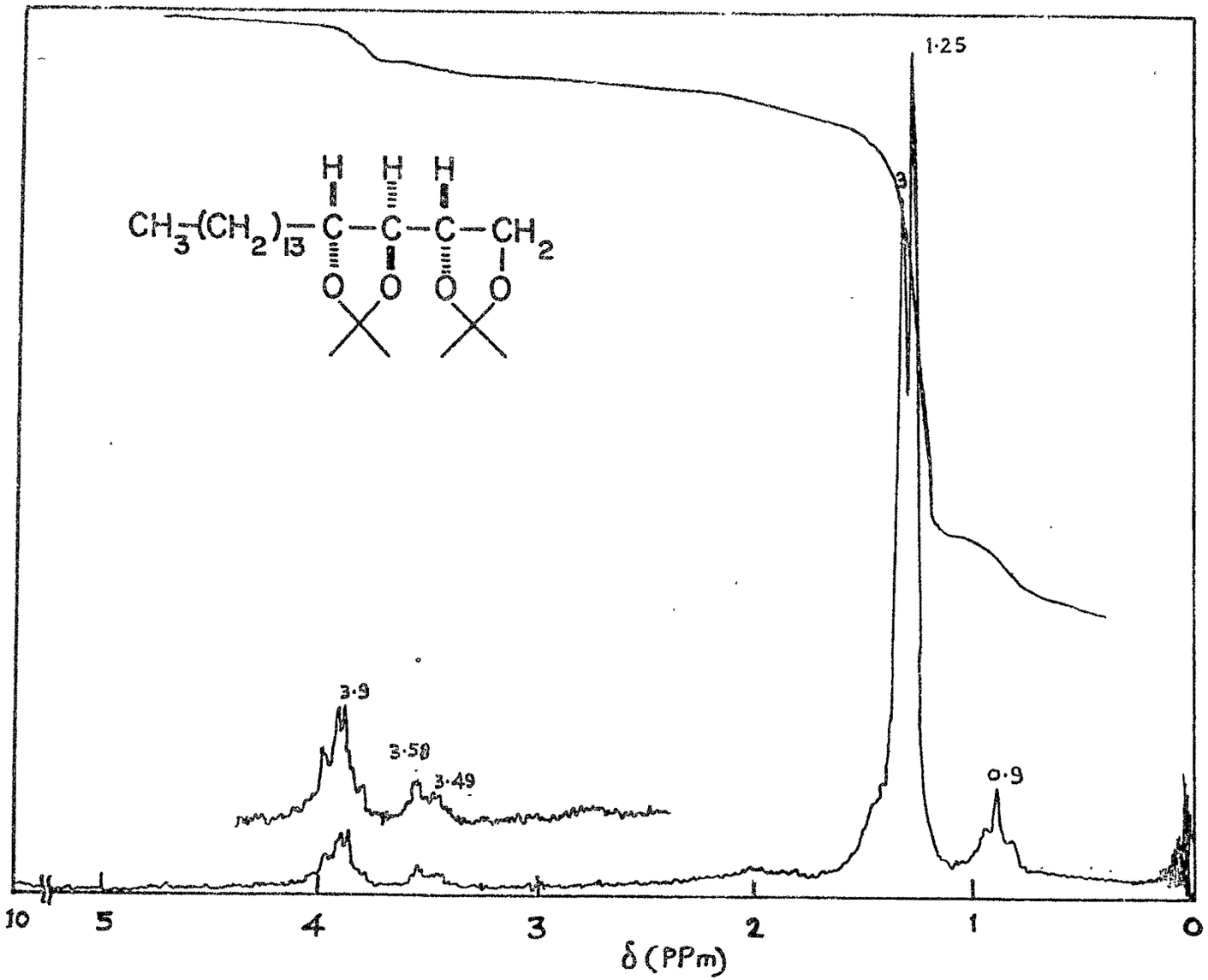


Fig. 37 - PMR Spectrum of 1,2;3,4-di-O-isopropylidene-D-xylo-1,2,3,4-octadecanetetrol (51)

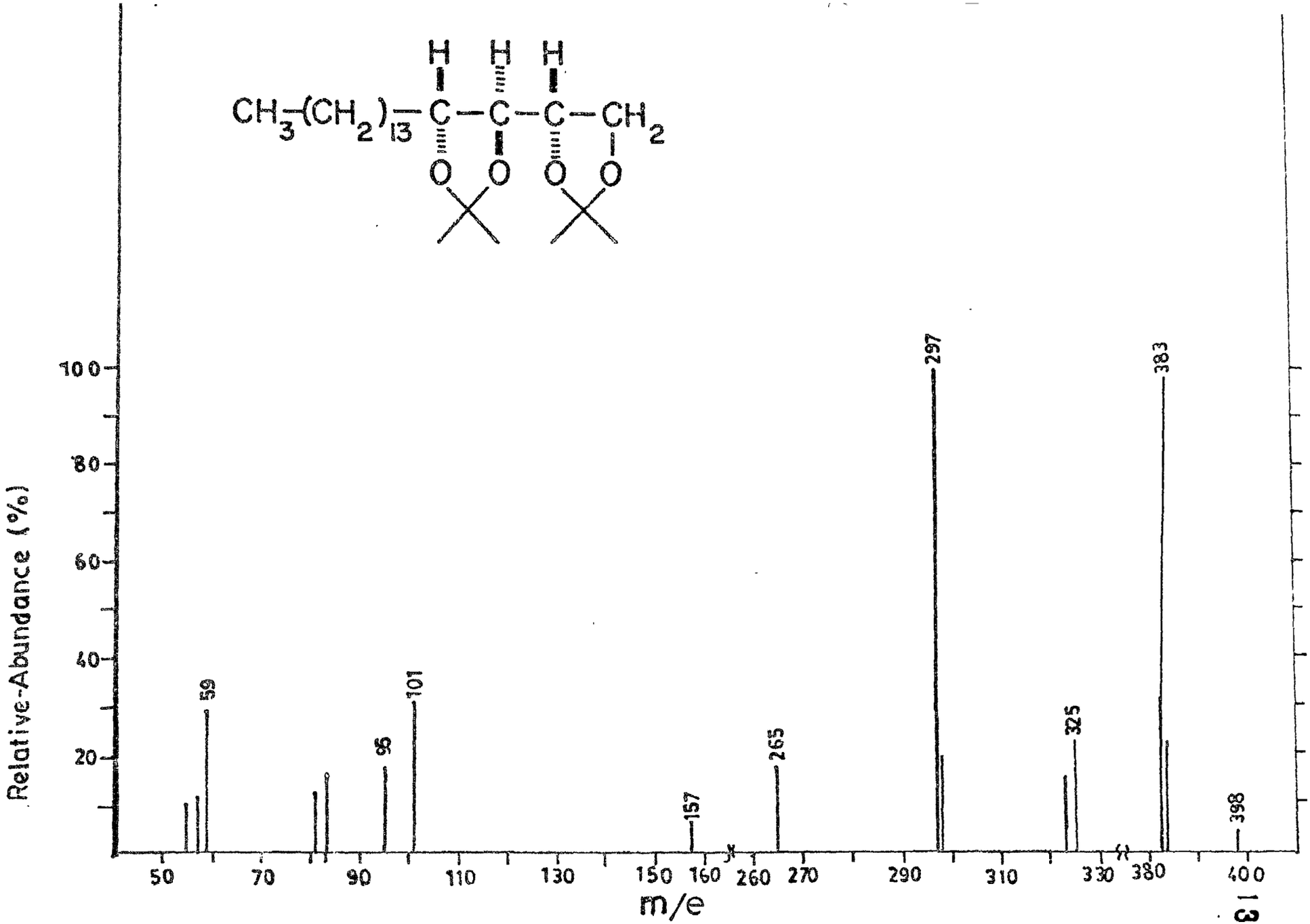


Fig. 38 - Mass Spectrum of 1,2;3,4-di-O-isopropylidene-D-xylo-1,2,3,4-octadecanetetrol (51)

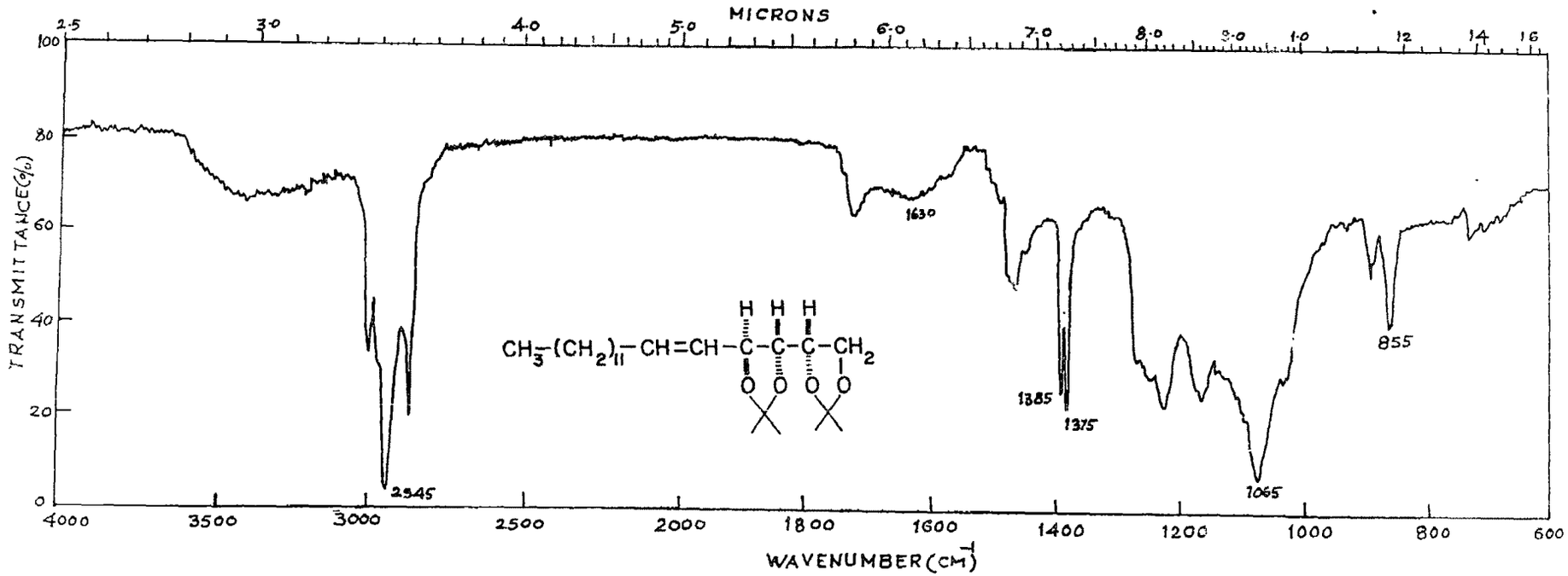


Fig. 39 - IR Spectrum of 1,2;3,4-di-O-isopropylidene-D-arabino-1,2,3,4-octadec-5-enetetrol (56)

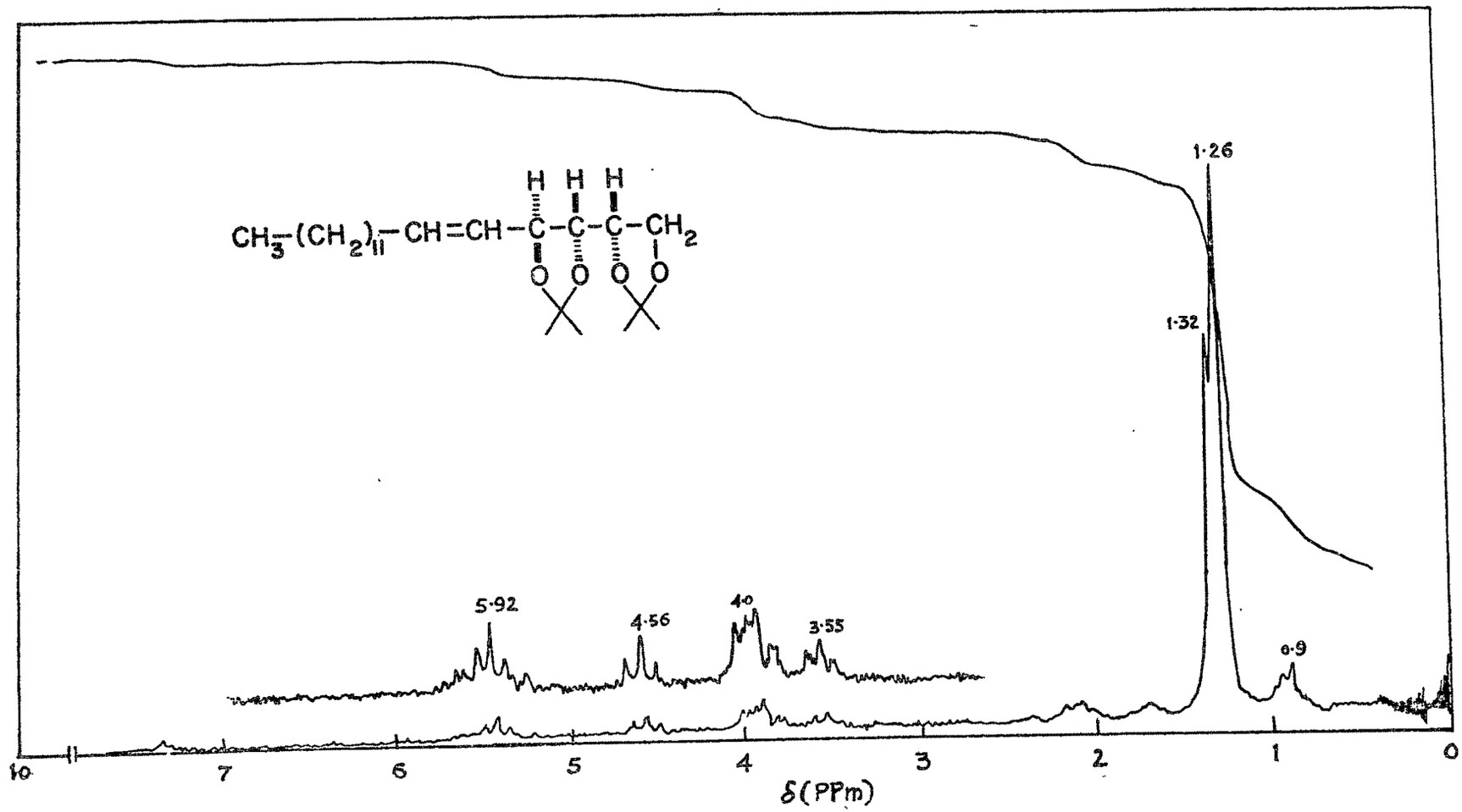


Fig. 40 :- PMR Spectrum of 1,2;3,4-di-O-isopropylidene-D-arabino-1,2,3,4-octadec-5-enetetrol (56)

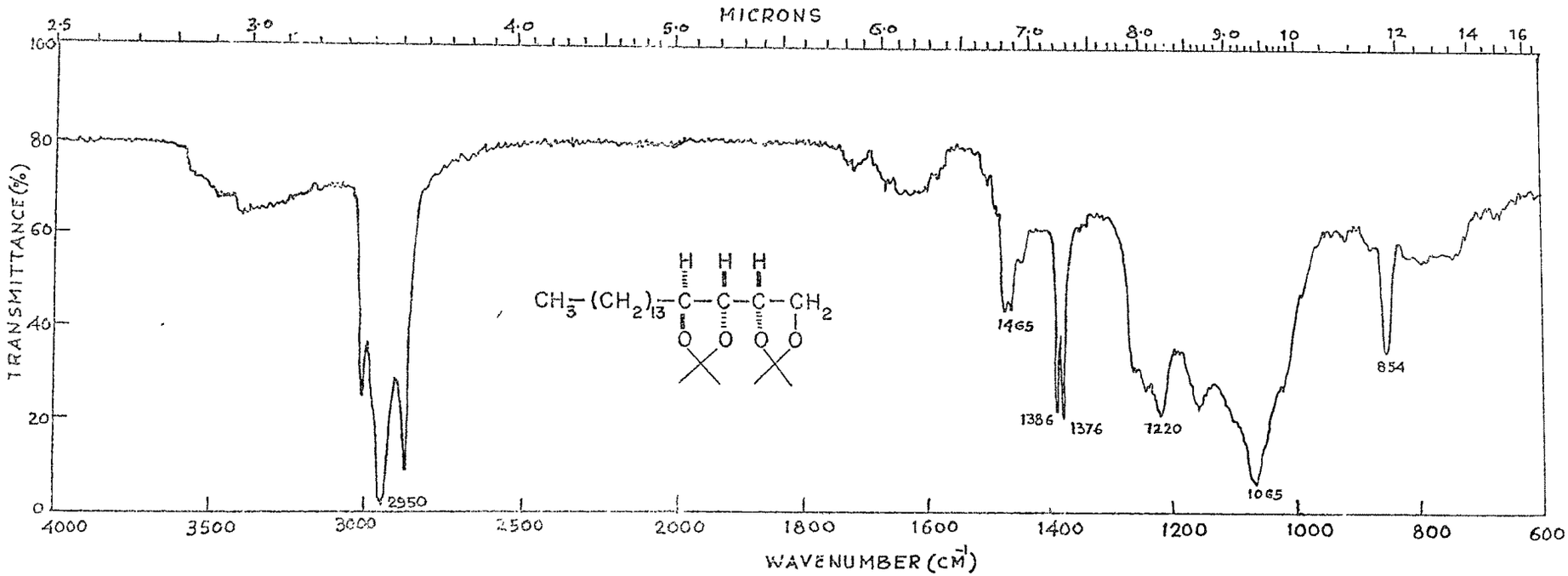


Fig. 41 - IR Spectrum of 1,2;3,4-di-O-isopropylidene-D-arabino-1,2,3,4-octadecanetetrol (57)

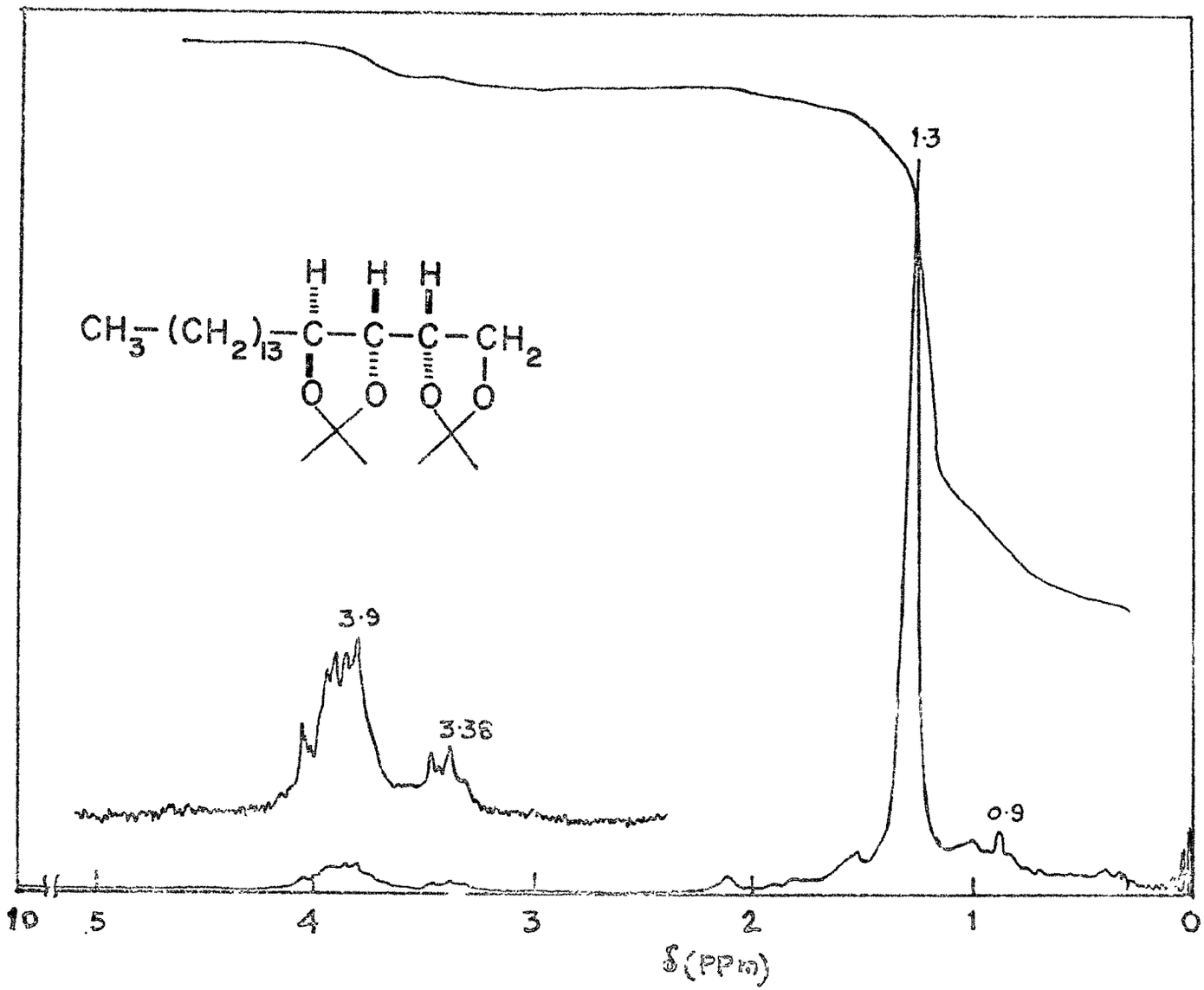


Fig. 42 - PMR Spectrum of 1,2;3,4-di-O-isopropylidene-D-arabino-octadecanetetrol (57)

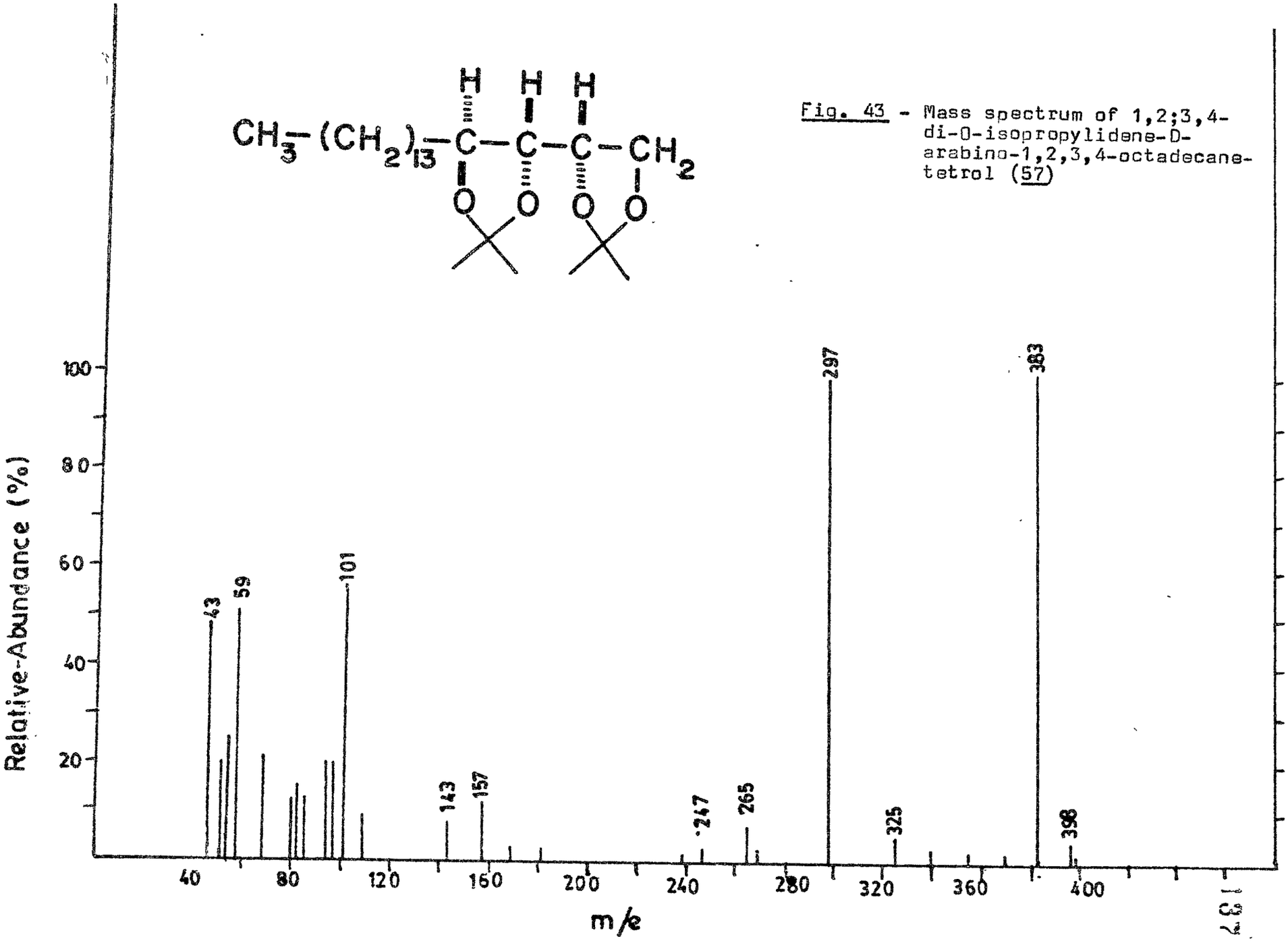


Fig. 43 - Mass spectrum of 1,2;3,4-di-O-isopropylidene-D-arabino-1,2,3,4-octadecanetetrol (57)

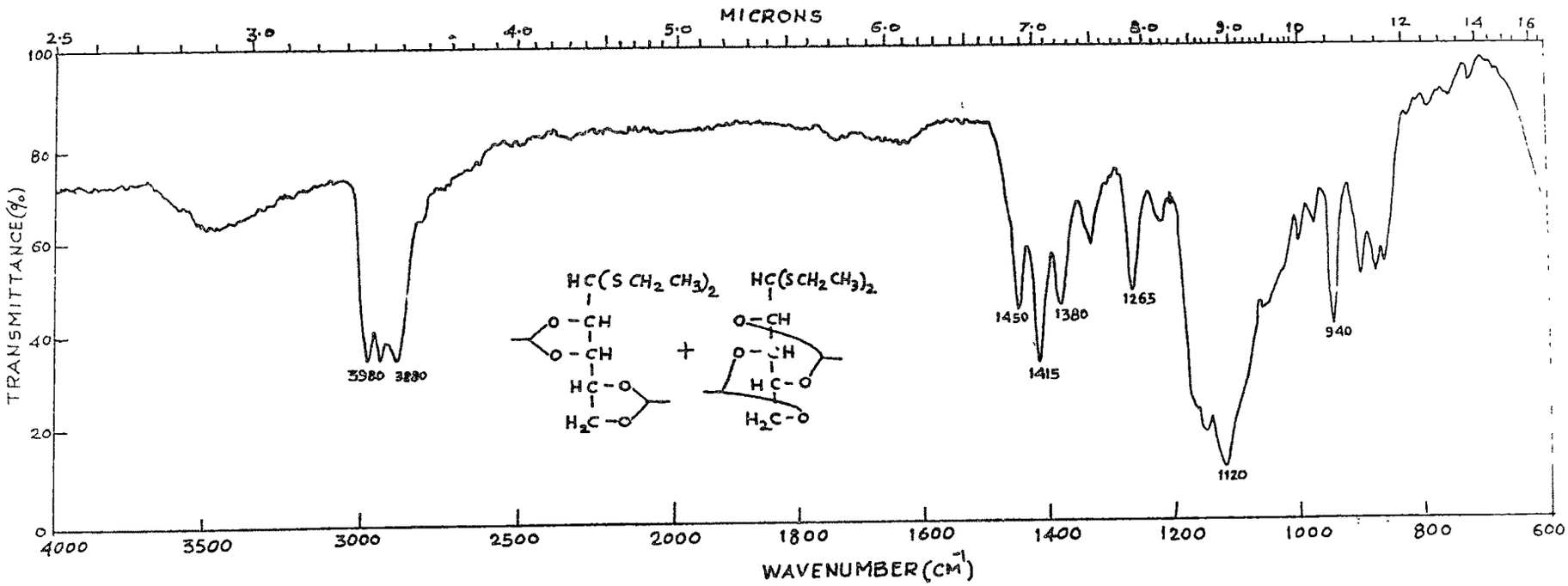


Fig. 44 - IR Spectrum of O-ethylidene-D-lyxosediethyl-dithioacetals (63)

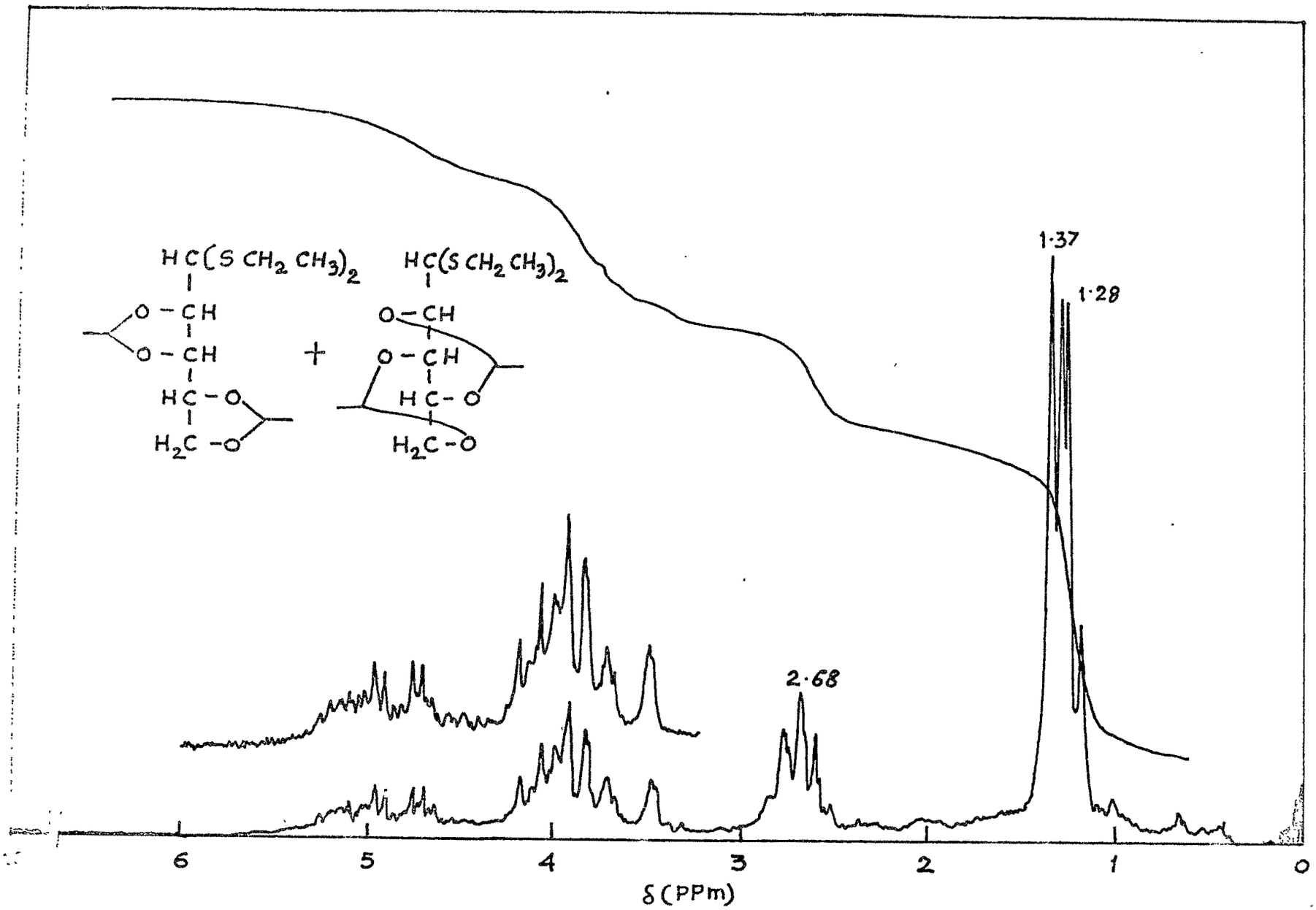


Fig. 45 - PMR Spectrum of O-ethylidene-D-lyxosediethyldithioacetals (63)

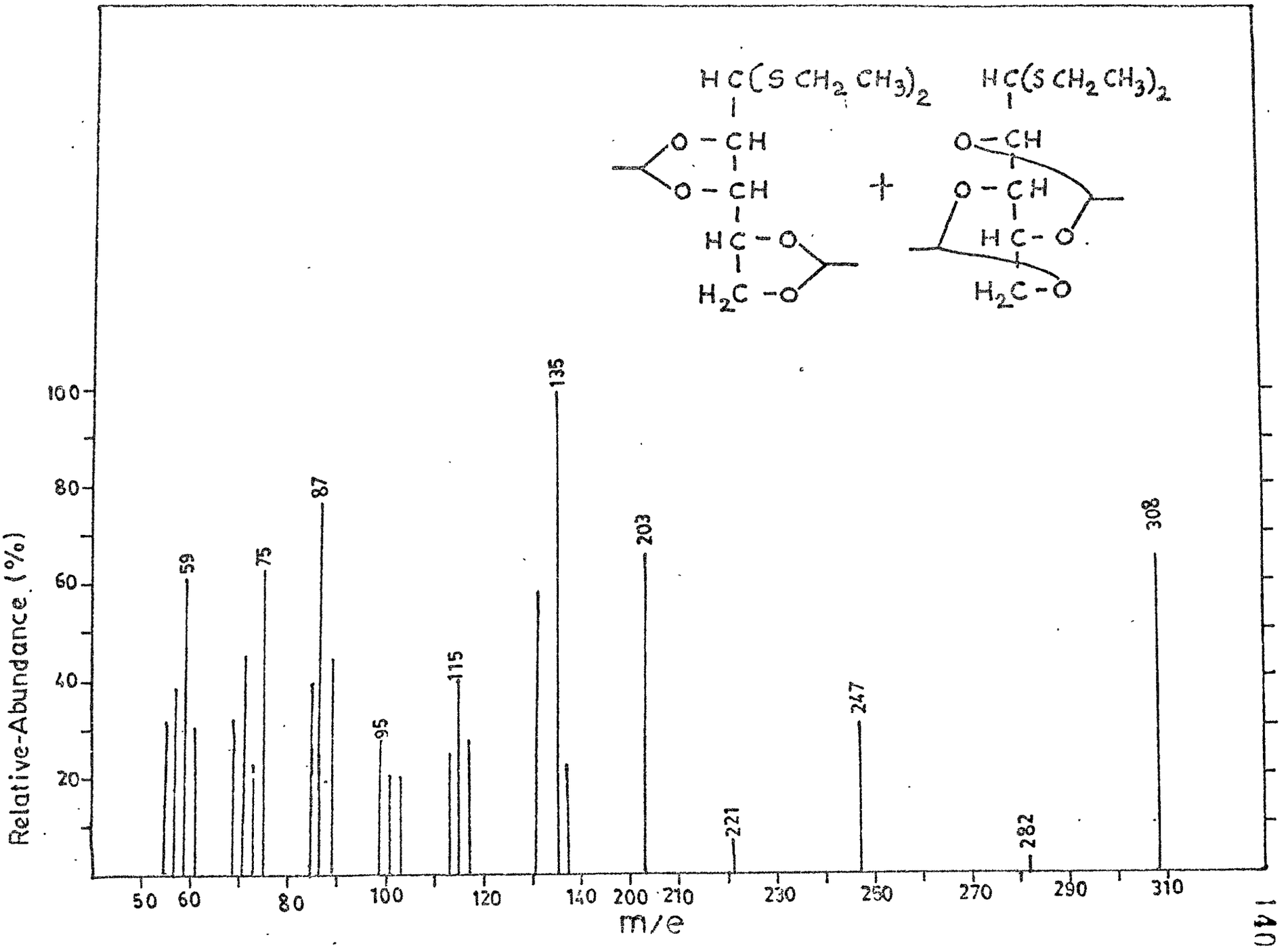


Fig. 46 - Mass Spectrum of O-ethylidene-D-lyxosediethyldithioacetals (63)

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