ACID CATALYZED REARRANGEMENTS OF CAROTANE (DAUCANE) SESQUITERPENOIDS

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ACID CATALYZED REARRANGEMENTS OF

CAROTANE (DAUCANE) SESQUITERPENOIDS

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TO STEVE, PENNY, HEIDI AND ADAM

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GLOSSARY OF ABBREVIATIONS

bp	boiling point
br	broad (IR)
C	centigrade
cm^{-1}	wave numbers (IR)
col	column
c	concentration, g/100 ml (ORD)
D_c	unit cell density (x-ray)
d	doublet (NMR)
g	gram
GC	gas chromatograph
glc	gas liquid chromatography
hr	hour
Hz	Hertz (cycles per second)
IR	infrared
J	coupling constant in Hz (NMR)
l	liter
δ	delta shift in ppm (NMR)
m/e	mass to charge ratio
mp	melting point
µg	microgram
µℓ	microliter
mg	milligram
ml	milliliter

min	minutes
m	multiplet (NMR)
NMR	nuclear magnetic resonance
ν	nu absorbancy in cm^{-1} (IR)
ORD	optical rotatory dispersion
ppm	parts per million (NMR)
q	quartet
R_f	ratio of the distance a compound moves to the distance the solvent moves (TLC)
R_t	retention time (GC)
sec	second
sh	shoulder (IR, NMR)
s	singlet
TLC	thin layer chromatography
tr	triplet (NMR)
V_c	unit cell volume (x-ray)
w	weak
z	number of molecules per unit cell (x-ray)

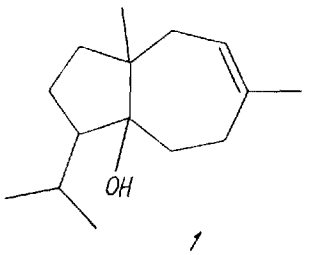
SUMMARY

During the early 1950's, Ruzicka rationalized the biogenetic relationships among terpenes in terms of the Biogenetic Isoprene Rule.[15] In order to verify some of the postulations, both *in vivo* and *in vitro* experiments have been performed. One type of study is to use laboratory reagents to transform one natural product to another. Since cationic cyclizations play a key role in the biogenesis of isoprenoids these rearrangements can be accomplished by acid catalysis to generate carbonium ions.

This thesis is concerned with the formic acid catalyzed rearrangement of the sesquiterpene carotol (1). To gain an understanding of this reaction in view of biogenetic postulations, the structures of new compounds were determined. Some studies were also conducted to gain a mechanistic understanding of the rearrangement.

During the formolysis of carotol (1) the initially formed daucene (9) and acoradienes (16) disappear and five other products which were detected by glc and separated by chromatography on silica gel are formed. These new compounds consist of two tricyclic olefins, tricyclodaucene (17) and isotricyclodaucene (18), daucane ether (19), tricyclocarotol (20) and tricyclocarotol formate (21). The structure of the tricyclocarotol skeleton 20, 21 was determined by examination

of spectral data and x-ray analysis of its p-iodobenzoate derivative 22. That of tricyclodaucene (17) was elucidated



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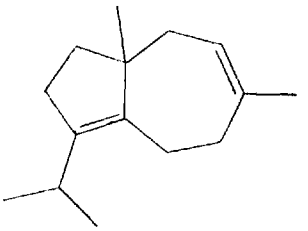

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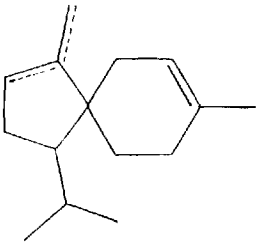

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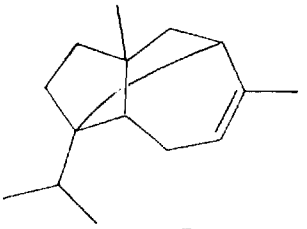

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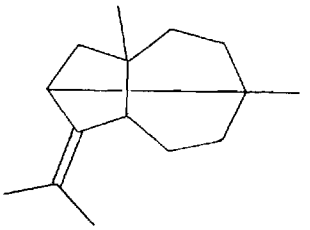

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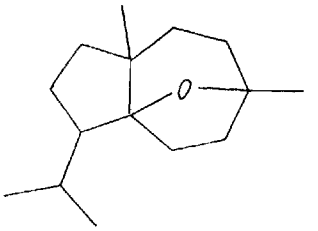

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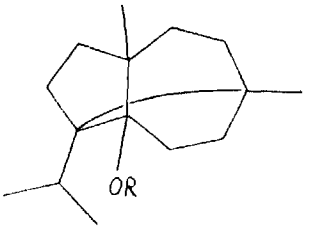
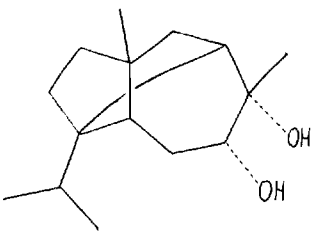


20 R = H

21 R = $\overset{O}{\overset{\|}{C}}-H$

22 R = $\overset{O}{\overset{\|}{C}}-Ar$



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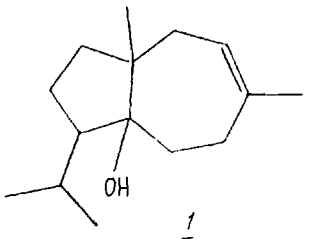
by spectral evidence from the olefin and several reaction products, then confirmed by the x-ray analysis of its cis diol 23. The structure of the second olefin, isotricyclodaucene (18), was determined from its spectral properties along with those of reaction and degradation products, while daucane ether (19) is assigned its structure from spectral evidence. In a series of ORD experiments, it was found that racemization took place during the first stages of the formolysis by way of the acoradienes (16). Also the tricyclocarotane products 20, 21 are the major constituents from one hour to six hours; then the olefins 17, 18 predominate. At six days, the major product is isotricyclodaucene (18).

CHAPTER I

INTRODUCTION

Carotol (1), a sesquiterpene with the daucane skeleton (2), is obtained as one of the predominant volatile components from the steam distillation of the seed of Daucus carota (Linn.) of the Umbelliferae family (wild or Indian black carrot). The constituents of carrot seed oil have been investigated by many workers verifying the presence of carotol (1).[1-4] Little work has been done on the volatile oil of carrot root. However, recently carotol (1) has also been found in the fruits of wild as well as cultivated carrots.[5-7]

Attempts to elucidate the correct structure for carotol (1) along with daucol (3), another daucane (2) in carrot seed oil, had been made since 1948.[2,8-10] However, the correct carbon skeleton was not proposed until 1959.[3,11,12] The configuration was determined soon after and verified by x-ray analysis of daucyl D,L-alanite hydrobromide (4).[13,14]



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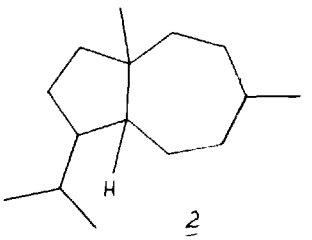

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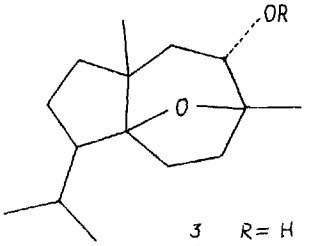


3 R = H

4 R = (CO)CH(CH$_3$)NH$_3^+$Br$^-$

Rationalization of the biogenetic relationships among the terpenes was made in the early 1950's by Ruzicka in terms of the Biogenetic Isoprene Rule.[15] In order to verify some of the postulations, experiments have been performed. One of the in vivo biosynthetic studies involving a sesquiterpene was done by Souček to determine the biogenetic path for the formation of carotol (1).

Theoretically, the daucane skeleton (2) could be derived from either cation 5 in Figure 1 which would involve a 1,3-hydride shift followed by an anti-Markownikoff cyclization and subsequent methyl migration to finally give 6 or by cyclization of cation 7 to give 8 followed by an overall 1,3-hydride shift and deprotonation to daucene (9). Specific hydration of this olefin 9 would give carotol (1).

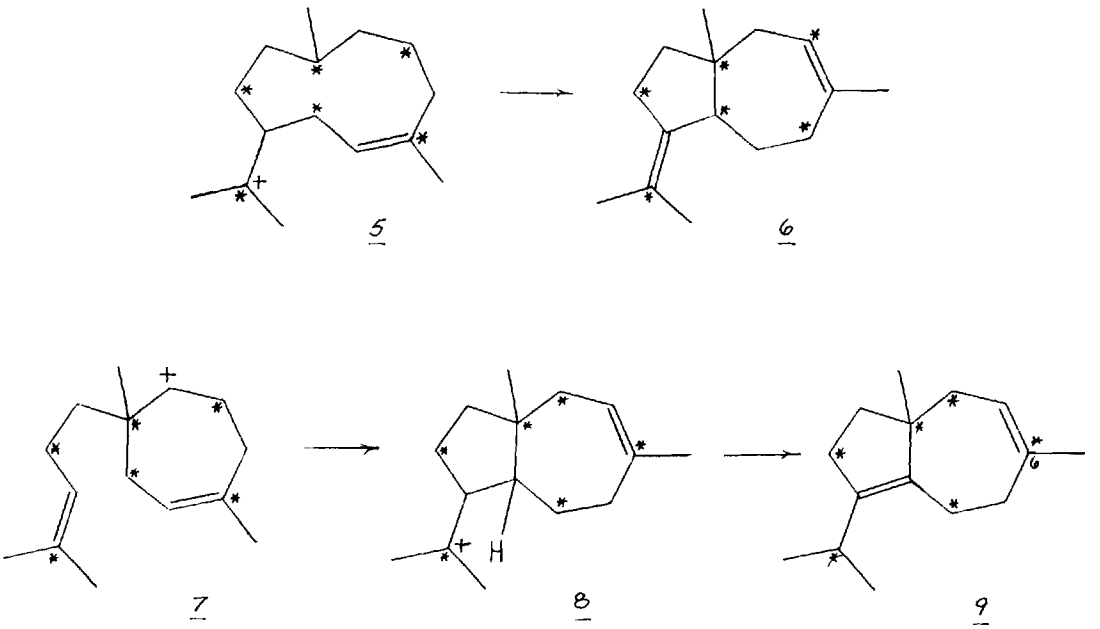
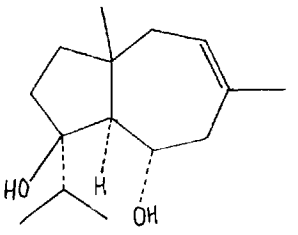


Figure 1. Postulated Pathways of Carotol (1) Formation

In a tracer study, Souček degraded carotol (1) obtained from carrot seeds of Daucus carota (Linn.) from plants which had incorporated [1-^{14}C]-acetate.[16] Since 1/6 of the molar activity was found at C6, the second pathway would be consistent with the labelling pattern in daucene (9).

Another group of sesquiterpenes represented by jaeschkeanadiol (10) also possess a daucane skeleton (2) but with a trans ring junction and could be derived biogenetically the same as carotol (1) except in the stereospecific hydration of daucene (9).[17]



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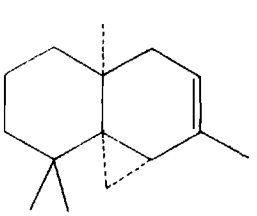
These biogenetic postulates have also stimulated the study of the transformation of one natural product to another using laboratory reagents. Since cationic cyclizations play a key role in the biogenesis of isoprenoids, these rearrangements can be accomplished by the generation of carbonium ions.[15] The acid catalyzed rearrangements of a variety of sesquiterpenes have been investigated. One of the most thoroughly studied has been thujopsene (11). Among the products formed using a variety of acidic conditions

were a mixture of α and β chamigrenes (12) which coocur with thujopsene in the leaf oil of Chamaecyparis taiwanensis and cupraene (13) which is also found with thujopsene in Hiba wood oil.



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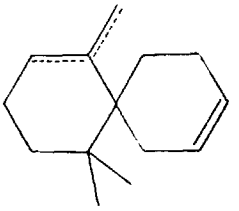

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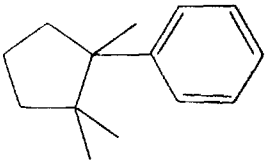

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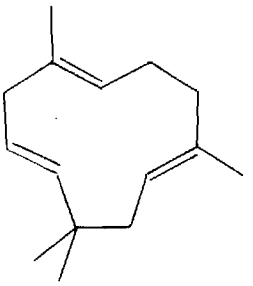
Another extensively studied acid catalyzed rearrangement has been that of humulene (14).[19] It is of particular interest because it can form the previously mentioned cation 5 which is theoretically the precursor to many naturally occurring sesquiterpenes including the daucanes (2).[15] Among the products formed are dienes with the bicyclodecane skeleton 15 similar to the daucanes (2) except for the placement of the methyl group in the seven membered ring.



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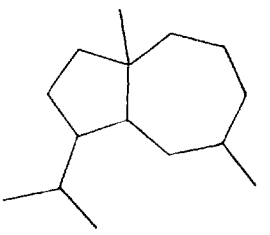

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The little work that has been done concerning the chemistry of daucanes (2) has been done on structure elucidation, the properties of epoxides and epoxy alcohols and the synthesis of daucene.[20-22] Recently Clower has described an investigation of the chemistry of these sesquiterpenes including the dehydration of carotol (1) with thionyl chloride.[23,24] He also reported that five major products: two olefins, an ether, an alcohol and a formate ester in addition to daucene (2) and acoradienes (16) were obtained from the acid catalyzed rearrangement of carotol (1). In view of the biogenetic postulations and the fact that some products from acid catalyzed rearrangements that have been discussed are found in plants, the purpose of this research was to characterize and elucidate the structures of the five compounds from the acid catalyzed rearrangement of carotol (1). Some studies on the interconversion of these products and reaction conditions were made to obtain information on the rearrangement's mechanism. Also an attempt was made to synthesize the daucane skeleton 2 by a biosimulated path as on Figure 1 from a cycloheptane cation.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

For spectral studies the following instruments and methods were used. All 60 mHz ^{1}H-NMR's were obtained using Varian Associates A-60D or T-60A spectrophotometers while 100 mHz and ^{13}C-NMR's were done on a JEOL PFT-100 Fourier transform spectrometer. Trimethylsilane was used as an internal standard. Infrared spectra were recorded using a Perkin-Elmer 237B spectrophotometer with solids in a nujol mull, potassium bromide pellets or in chloroform solution while liquids were in the form of a thin film on sodium chloride plates or in chloroform solution. The bands at 2850 and 1601 cm^{-1} of a polystyrene film were used as reference points. Mass spectral data were obtained using either an Hitachi Perkin-Elmer (Model RMU-7L) or a Varian (Model M66) spectrophotometer both with electron beam energy of 70 eV, while optical rotatory dispersion curves were obtained using a JASCO ORD/UV-5 spectrophotometer.

Physical separations were performed according to the following methods. Gas liquid chromatographs were obtained on either a Hewlett-Packard Model 402 or F and M Model 400 gas chromatographs using flame ionization detectors. All columns contained 100/120 Gas Chrom Q support in glass,

U shaped columns and are as follows:

Column Number	Liquid Phase	Support	Column Size
I	5% SE30	100/120 Gas Chrom Q	6'x1/4"
II	5% SE30	100/120 Gas Chrom Q	4'x1/4"
III	2% SE30	100/120 Gas Chrom Q	6'x1/4"
IV	3% SE30	100/120 Gas Chrom Q	4'x1/4"
V	15% SE30	100/120 Gas Chrom Q	6'x1/4"

Thin layer chromatography was performed on precoated silica gel plates (13181, Eastman Kodak). The R_f values were obtained by taking the ratio the spot moved to the distance of the solvent front. Dection was by iodine vapor. Column chromatography was performed using the following adsorbents: silica gel (100-200 mesh), neutral or acid washed alumina oxide deactivated with water.

Melting points are uncorrected and done on either a Thomas-Hoover capillary melting point apparatus or Thomas Kofler micro hot stage Model 651. While solvents were removed in vacuo on a Büchler Instruments rotary evaporator at water aspirator pressure. Microanalyses were done by Atlantic Microlabs, Atlanta, Georgia.

For ozonolyses a Welsbach (Model 408) Ozonator was used. X-ray data were collected on a Syntex P_{21} Diffractometer.

Analytical samples of oils were obtained by bulb to bulb distillation or short path distillation which is referred to as hot box distillation in this thesis.

CHAPTER III

EXPERIMENTAL

Purification of Carotol (1)

Carotol (1) used for the following research was obtained from carrot seed oil from two sources, P. Robertet and Co., Grasse, France and Fritzshe Dodge and Olcott Inc., New York. It was purified by distillation on a Nester-Faust annular teflon spinning band column (24 x 0.5 inches). The carotol fraction (bp 84°C/0.23 mm) was 96% pure by glc analysis (Col I, 110°C, R_t = 20 min). The spectral data which follows agrees with that previously obtained.[24]

bp 77-78°C/0.03 mm

IR: ν_{neat} (cm^{-1}): 3600, 3500.

^{1}H-NMR (δ,$CDCl_3$): 0.95 (s,3H); 0.96 (d, J = 6 Hz, 3H); 1.02 (d, J = 6 Hz, 3H); 1.18 (s,1H); 1.65 (s,3H); 5.40 (m,1H).

^{13}C-NMR (δ,$CDCl_3$): 137.7 (=$\underline{C}(R)_2$), 121.5 (=$\underline{C}\begin{smallmatrix}R\\H\end{smallmatrix}$), 84.0 ($\underline{C}$-O), 48.8 (quaternary) 52.2, 39.3, 38.5, 34.2, 29.3, 27.4, 25.1, 24.3, 23.9, 21.3.

Mass spectrum: M^+ = 222 (2%), m/e = 161 (100%)

ORD (c = 3.88, $CHCl_3$): $[\phi]_{700}$ = 40.0°, $[\phi]_{589}$ = 57.2° ($[\alpha]_{589}$ = 25.8°), $[\phi]_{500}$ = 80.1°, $[\phi]_{400}$ = 131.6°, $[\phi]_{300}$ = 246.0°.

Determination of GLC Response Factors

The standard solution of olefins 17, 18, ether 19, alcohol 20 and formate 21 were prepared by adding weighed quantities of each to volumetric flasks and addition of hexane to the mark. Then measured samples were injected into the GC (Col I, 160°C, detector 210°C) and the area of the peaks were determined to give the response factors as shown in Table 1. For the quantitative experiments in this thesis the areas were multiplied by the ratios to correct for the different responses of the compounds.

Five Day Formolysis of Carotol (1) at 25°C

A solution of carotol (1) (3.0g, 13 mmoles) in 90% formic acid (200 ml) was stirred at 25°C for 5 days. The reaction was stopped by the addition of saturated salt solution (200 ml). The aqueous solution was extracted with ether (3 x 100 ml). The combined ether fractions were washed with water (5 x 50 ml), followed by saturated potassium bicarbonate solution until basic to litmus and then neutral to litmus with water. After drying over magnesium sulfate, the extracts were filtered and evaporated *in vacuo* to give a brown oil (3.5g).

Glc analysis (Col I, 160°C) showed four major peaks and several minor peaks. Table 2 shows the percentages of the main products. The major components were separated by chromatography on silica gel (320g), while no attempt was

Table 1. GLC Response Factors*

Compound	Concentration (mg/ml)	Injection (µℓ)	Injection (µg)	Area (cm^2)	Weight/Area (µg/cm^2)	Response Factor
Olefins 17,18	0.70	0.5	0.36	0.76	0.48	1.0
		1.0	0.70	1.4	0.50	
		2.0	1.40	2.4	0.58	
				Average	0.52	
Ether 19	0.30	0.5	0.15	0.3	0.50	1.3
		1.0	0.30	0.4	0.75	
		2.0	0.60	0.8	0.75	
		3.0	0.90	1.5	0.60	
				Average	0.65	
Alcohol 20	1.1	0.2	0.22	0.6	0.37	1.0
		0.4	0.44	1.0	0.44	
		0.6	0.66	1.2	0.55	
		1.0	1.1	1.8	0.61	
				Average	0.49	
Formate 21	1.1	1.0	1.1	1.7	0.65	1.4
		2.0	2.2	3.0	0.73	
		1.5	1.7	2.3	0.74	
				Average	0.70	

*Col I, 160°C, detector 210°C

Table 2. Percentages of Major Products* from Formolysis of Carotol, 25°C

Days	Olefins 17,18	Ether 19	Tricyclo-carotol (20)	Tricyclocarotol Formate (21)
5	15.3	14.6	36.4	34.6
11	19.9	15.8	31.9	32.5
14	27.5	22.6	30.5	19.4
42	42.8	19.3	26.0	11.9

*See Table 1 for response factors.

made to separate the minor constituents. Fraction one (503 mg, hexane eluent) contained one peak by glc (Col I, 160°C, R_t = 1 min). However, glc at a lower temperature (125°C) showed two peaks (R_t = 4 min 45 sec and R_t = 5 min 2 sec). These peaks corresponded to the two olefins 17 and 18 which were present in the ratio of 1.0 to 0.4.

Then, the second major fraction (286 mg, hexane-benzene 1:1 eluent) was identified as ether 19 by comparison of its glc (Col I, 160°C, R_t = 1 min 36 sec) and that of previously characterized ether 19.[24] The following spectral and physical properties were previously observed for ether 19;[24] and the IR, ^{1}H-NMR and mass spectrum are on Plates I, II and III of the Appendix.

bp 44-47°/0.1 mm (hot box).

IR: ν_{neat} (cm^{-1}): 1110, 1040.

^{1}H-NMR (δ,$CDCl_3$): 0.73 (3H,s); 0.85 (3H,d,J = 6 Hz); 1.13 (3H,d,J = 6 Hz); 1.22 (3H,s).

^{13}C-NMR (δ,$CDCl_3$): 92.8, 77.3 (ether carbons); 44.0 (quaternary carbon), 47.4, 34.2, 32.2, 29.6, 27.3, 26.7, 26.0, 22.8, 22.1.

Mass spectrum: M^+ = 222 (43%), m/e 179 (100%).

ORD (c = 3.39, $CHCl_3$): $[\phi]_{700}$ = -27.9°, $[\phi]_{600}$ = -33.6°, $[\phi]_{589}$ = -39.1°, ($[\alpha]_{589}$ = -17.6°), $[\phi]_{500}$ = -50.3°, $[\phi]_{400}$ = -89.5°, $[\phi]_{300}$ = -195°.

The fourth product (718 mg, hexane-benzene 1:1 eluent), which was obtained pure, was tricyclocarotol formate (21) which was compared by glc analysis, (Col I, 160°C, R_t = 5 min 26 sec) with previously characterized formate 21.[24] The spectral and physical properties were as follows:

bp 83-87°C/0.1 mm (hot box).

IR: ν_{neat} (cm^{-1}): 1730, 1180, 1150.

^{1}H-NMR (δ,$CDCl_3$): 0.83 (3H,s); 0.97 (3H,s); 0.98 (3H,d, J = 7 Hz); 8.13 (1H,s).

^{13}C-NMR (δ,$CDCl_3$): 101.1 (C-O), 160.2 (HCO_2-), 61.8, 50.0, 45.9 (quaternary carbons), 37.6, 37.1, 36.0, 32.2, 29.8, 28.3, 23.7, 21.8, 21.0, 19.8.

Mass spectrum: M^+ not observed, M^+ -HCOOH = 204 (34%); m/e = 161 (100%).

ORD (c = 4.52, $CHCl_3$): $[\phi]_{700}$ = 48.9°, $[\phi]_{600}$ = 66.4°, $[\phi]_{589}$ = 71.9°, ($[\alpha]_{589}$ = 28.8°), $[\phi]_{500}$ = 99.5°, $[\phi]_{400}$ = 176.9°, $[\phi]_{300}$ = 365°.

The next fraction (1.09g, hexane-benzene 1:1 eluent) was a mixture of tricyclocarotol formate (21) and tricyclocarotol (20), while the last pure fraction was shown by glc (Col I, 160°C) to contain tricyclocarotol (20) (R_t = 3 min 12 sec). This was further purified by sublimation (25°C/0.1 mm) to give white granular crystals, mp 46-47°C. The glc and spectral properties obtained for this compound agree with those of Clower.[24] The observed spectral properties were as follows and the IR, ^{1}H-NMR and mass spectrum appear on Plates IV, V and VI of the Appendix.

IR: ν_{neat} (cm^{-1}): 3250-3600, 1070, 1020.

^{1}H-NMR (δ,$CDCl_3$): 0.85 (3H,s); 0.93 (3H,s); 1.02 (3H,d, J = 6 Hz); 1.15 (3H,d,J = 6 Hz); 1.42 (1H,m).

^{13}C-NMR (δ,$CDCl_3$): 91.7 (hydroxyl carbon); 60.2, 48.5, 47.4 (quaternary carbons), 38.3, 36.6, 36.2, 35.9, 32.5, 30.9, 30.1, 24.1, 21.0, 19.8.

Mass spectrum: M^+ = 222 (6%), m/e = 179 (100%).

ORD (c = 3.57, $CHCl_3$): $[\phi]_{700}$ = 38.5, $[\phi]_{589}$ = 53.3° ($[\alpha]_{589}$ = 24.0°), $[\phi]_{500}$ = 77.0°, $[\phi]_{400}$ = 133.2°, $[\phi]_{300}$ = 295.3°.

Several experiments were conducted at 25°C varying the length of time of formolysis. The product composition of these as determined by peak area of glc tracings appear in Table 2.

Separation of Tricyclodaucene (17) and Isotricyclodaucene (18)

The olefins 17, 18 (503 mg) were separated on 25% silver nitrate-silica gel (50g) column eluting with distilled olefin free petroleum ether (bp 30-50°C). Tricyclodaucene (17) (199 mg) was obtained pure as determined by glc (Col I, 125°C, R_t = 4 min 45 sec). The glc and ^{1}H-NMR agree with those previously reported.[24] The next fraction (33 mg) contained a mixture of the two olefins, while the third fraction (74 mg) contained pure isotricyclodaucene (18) as shown by glc (Col I, 125°C, R_t = 5 min 2 sec) with glc, ^{1}H-NMR and IR that agree with those of previously isolated material.[24] Stripping the silica gel column with ether-petroleum ether (1:9) gave a mixture (90 mg) of the olefins and unknowns.

The spectral and physical properties of the olefins are as follows and the IR, ^{1}H-NMR and mass spectrum appear on Plates VII to XII of the Appendix.

Tricyclodaucene (17)

bp 45°/0.05 mm (hot box).

IR: ν_{neat} (cm^{-1}): 1450, 1375, 810.

^{1}H-NMR (δ,$CDCl_3$): 0.72 (3H,d,J = 6 Hz); 0.90 (3H,d,J = 6 Hz); 1.00 (3H,s); 1.62 (3H,m); 5.07 (1H,m).

^{13}C-NMR (δ,$CDCl_3$): 142.4 (disubstituted olefinic carbon), 116.2 (monosubstituted olefinic carbon), 52.5 (quaternary carbon), 48.1, 47.6, 47.3, 46.9, 39.7, 26.5, 24.3, 22.8, 18.6.

Mass spectrum: M^+ = 204 (35%), m/e = 123 (100%).

ORD (c = 3.01, $CHCl_3$): $[\phi]_{700}$ = 54.3°, $[\phi]_{600}$ = 74.5°, $[\phi]_{589}$ = 81.2° ($[\alpha]_{589}$ = 39.8°), $[\phi]_{500}$ = 122°, $[\phi]_{400}$ = 210°, $[\phi]_{300}$ = 576°.

Analysis ($C_{15}H_{24}$): calculated: C, 88.24; H, 11.76.
found: C, 88.17; H, 11.74.

Isotricyclodaucene (18)

bp 90°C/0.3 mm (hot box).

IR: ν_{neat} (cm^{-1}): 1450, 1375.

^{1}H-NMR (δ,$CDCl_3$): 0.86 (3H,s); 0.98 (3H,s); 1.58 (3H,s); 1.62 (3H,d, J = 1 Hz); 2.28 (1H,br); 2.76 (1H,br).
Irradition at: 137.0 Hz; 1.62 (3H,s).
165.5 Hz; 1.62 (3H,d).

^{13}C-NMR (δ,$CDCl_3$): 141.9, 118.0 (olefinic carbons), 41.9, 32.6 (quaternary carbons), 47.2, 46.5, 45.7, 39.6, 38.9, 35.1, 32.0, 26.5, 21.4, 20.3, 19.3.

Mass spectrum: M^+ = 204 (100%).

ORD (c = 1.16, $CHCl_3$): $[\phi]$ = 74.6°, $[\phi]_{589}$ = 124° ($[\alpha]_{589}$ = 60.8°), $[\phi]_{500}$ = 178.0°, $[\phi]_{400}$ = 292.8°, $[\phi]_{300}$ = 344.4°.

Analysis ($C_{15}H_{24}$): calculated: C, 88.24; H, 11.76.
found: C, 88.21, H, 11.71.

Six Day Formolysis of Carotol (1) at 45°C

A solution of carotol (1) (3.0g, 0.13 mmoles) in 90% formic acid (200 ml) was stirred at 45°C for six days and the reaction was worked up the same way as for the five day

formolysis at 25°C to give a brown oil (3.0g).

Glc analysis (Col I, 140°C) showed one major peak corresponding to the olefin mixture 17, 18 and was 72% of the product's composition. While the remaining peaks and their percent compositions were daucane ether (19) 12%, tricyclocarotol (20) 9% and tricyclocarotol formate (21) 7%. The oelfins 17, 18 were separated from the minor products by chromatography on silica gel (280g). Elution with hexane gave a mixture (1.54g) which was shown by glc analysis (Col I, 120°C) to contain tricyclodaucene (17) 15% and isotricyclodaucene (18) 85%. No attempt was made to separate the other constituents.

Lithium Aluminum Hydride Reduction of the Tricyclocarotol Formate (21) in a Mixture with Tricyclocarotol (20)

A mixture (1.9g) containing tricyclocarotol formate (21) (4.8 mmoles) and tricyclocarotol (20) (3.0 mmoles) was dissolved in anhydrous ethyl ether (100 ml). After cooling the solution to 0°C, lithium aluminum hydride (3.8g, 100 mmoles) was added and stirring was continued at 0°C for 10 minutes and at 25°C for 2.5 hours. Then, excess lithium aluminum hydride was destroyed by cautiously adding small pieces of ice followed by water (50 ml). The solution was stirred until no gray color remained.

The ether layer was separated and the aqueous fraction was extracted with ether (3 x 50 ml). The combined ether

fractions were washed with water (3 x 50 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo*. The light yellow oil (1.6g) was shown to be 96% pure by glc analysis (Col IV, 160°C) with glc retention time, ^{1}H-NMR, IR and mass spectra identical to those of authentic tricyclocarotol (20).

Conversion of Carotol (1) into Daucene (9) and Acoradienes (16) with Thionyl Chloride[23]

A solution of thionyl chloride (1.2 ml, 16.3 mmole) in dry pyridine (16 ml) was added to carotol (1) (1.00g, 4.54 mmole) at 0°C over 10 minutes. After stirring for 10 minutes, the reactants were poured over ice (20g) and diluted with water (100 ml) and the product was extracted with ether (200 ml total). Then, the combined ether extracts were washed with 10% hydrochloric acid solution until acidic, neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield an oil (900 mg) which was determined to be 17% of an acoradiene mixture (16) and 83% daucene (2) by glc (Col IV, 125°C).

The product (1.7g) from two reactions were combined and chromatographed on 25% silver nitrate impregnated silica gel (170g) eluting with distilled olefin free petroleum ether. The first fraction (249 mg) contained the acoradiene mixture (16), the second a mixture (567 mg) of acoradienes (16) and daucene (9) and a third pure daucene (9).

Identification of the acoradienes (16) was made by glc analysis (Col IV, 125°C) of the product and an authentic sample along with an ^{1}H-NMR spectrum of the mixture which had the following features (δ,$CDCl_3$): 0.77-1.10 (complex multiplet, methyls); 1.53-1.78 (complex multiplet, olefinic methyls); 5.25-5.52 (multiplet, olefinic protons).

Daucene (9) showed the following spectral properties which were identical to those reported in the literature:[23]

bp: 100°C/0.3 mm (hot box).

IR: ν_{neat} (cm^{-1}): 3030, 830.

^{1}H-NMR (δ,$CDCl_3$): 0.80 (d, J = 6 Hz, 3H); 0.90 (d, J = 6 Hz, 3H); 1.57 (s, olefinic methyls, 6H); 5.30, 5.37 (olefinic protons, 1H each).

^{13}C-NMR (δ,$CDCl_3$): 142.0, 139.5, 138.7, 122.7 (olefinic); 49.6 (quaternary); 40.5, 38.7, 33.7, 27.3, 26.5, 25.8, 23.6, 22.6, 21.8, 21.2.

Mass spectrum: M^+ = 204 (13%), m/e = 94 (100%).

ORD (c = 4.45, $CHCl_3$): $[\phi]_{600}$ = 68.8°, $[\phi]_{589}$ = 73.2° ($[\alpha]^{25}_{589}$ = 35.9°), $[\phi]_{500}$ = 100.0°, $[\phi]_{400}$ = 165.0°.

Conversion of Carotol (1) into Daucene (9) with Formic Acid

Carotol (266 mg, 1.20 mmole) was stirred with 90% formic acid for 30 minutes at 45°C. After working the reaction up as previously described for formolyses, pure daucene (9) (58 mg) was obtained from chromatography on 25% silver nitrate impregnated silica gel as previously described. The spectral

properties, including ORD, were the same as those reported above for daucene (9) obtained from the thionyl chloride reaction.

Studies on the Racemization of Tricyclocarotol (20)

Carotol (1) (1.7g, 10.0 mmoles) was stirred in 90% formic acid (100 ml) at room temperature for 2 days. After working the reaction up as already described above for formolyses, the product (1.8g) was chromatographed on silica gel (180g). The combined tricyclocarotol (20) and tricyclocarotol formate (21) fraction (benzene-hexane 1:1 eluent) was stirred with lithium aluminum hydride as previously described. After determination of its ORD and ^{1}H-NMR spectra, the tricyclocarotol (20) (324 mg) was returned to 90% formic acid (20 ml).

Half of the above reaction mixture was worked up in 12 days (total reaction 14 days) and the remainder in 36 days (total reaction 38 days) by the same procedure as described above. The results from the ORD measurements of hot box distilled tricyclocarotol (20) appear in Table 3.

ORD of Tricyclocarotol (20) Obtained from Formolysis of Acoradiene Mixture (16)

The acoradiene mixture (16) (182 mg, 0.89 mmole) was stirred with 90% formic acid (10 ml) at room temperature for a total of five days. After four hours, glc analysis (Col IV, 125°C) showed that the acoradienes (16) had not

Table 3. ORD Measurements of Tricyclocarotol 20 Formolyses with Different Starting Compounds

Starting Compound	Time, days*	c, $CHCl_3$	$[\phi]_{700}$ °	$[\phi]_{589}$ °	$[\alpha]_{589}$ °	$[\phi]_{500}$ °	$[\phi]_{400}$ °	$[\phi]_{300}$ °
Carotol (1)	5	3.6	38.5	53.3	24.0	77.0	133.2	295.3
Carotol (1)	2	3.7	11.8	24.0	10.8	35.5	62.8	149.8
Tricyclo-carotol (20)**	12	5.3	18.6	26.8	12.1	41.3	70.2	171.2
Tricyclo-carotol (20)**	36	3.8	25.3	24.8	11.2	35.0	73.0	146.0
Daucene (9)	10	2.9	54.2	77.4	34.8	108.1	185.6	402.2
Acoradienes (16)	5	3.2	0.00	0.00	0.00	3.46	3.46	10.4

*All done at 25°C

**Tricyclocarotol from 2 day formolysis used for these reactions.

reacted. In three days, there was 30.4% combined olefins 17, 18, 15.0% ether 4, 24.9% tricyclocarotol (20) and 21.9% tricyclocarotol formate (21). These proportions did not change in five days so the reaction was worked up and chromatographed as previously described. The combined alcohol 20-ester 21 fraction (93.8 mg) was stirred with lithium aluminum hydride as usual to yield after hot box distillation (120-130°C/0.5 mm) a solid (mp 40°C) which was identical to tricyclocarotol (20) obtained from carotol (1) formolysis by glc analysis (Col IV, 160°C) and ^{1}H-NMR. However, as the results in Table 3 show, the tricyclocarotol (20) had been racemized.

ORD of Tricyclocarotol (20) Obtained from Formolysis of Daucene (9)

Daucene (2) (251 mg, 1.23 mmole) was stirred with 90% formic acid (20 ml) at room temperature for ten days. After working the reaction up as usual, analysis by glc (Col V, 140°C) showed that there was 36.3% of the olefin mixture 17, 18, 18.8% of the ether 19, 33.4% of tricyclocarotol (20) and 11.5% of tricyclocarotyl formate (21). Reduction of the formate 21 (81.9 mg) in a mixture with alcohol 20 obtained from silica gel chromatography yielded pure tricyclocarotol (20) (78.1 mg) which was the same by glc (Col V, 140°C) and ^{1}H-NMR as that obtained from the formolysis of carotol (1). The results of the ORD measurement of the hot box distilled alcohol 20 appear in Table 3.

Optically Active ^{1}H-NMR Shift Study of Tricyclocarotol (20)

Tricyclocarotol (20) (38.7 mg, 0.16 mmole) was dissolved in carbon tetrachloride containing TMS. Europium tris-[3-(trifluoromethylhydroxymethylene)-d-camphorato] Aldrich, #17, 649-4, 0.4 mmole/1.0 ml, CCl_4) was added to the alcohol 20 in 0.02 mmole increments. After each addition the ^{1}H-NMR spectrum was recorded. The most separation of methyl peaks occurred after the addition of 0.13 mmoles of shift reagent. However, it was not possible to determine the proportion of enantiomers from the results. The signals from the methyls obtained from the sample with 0.13 mmoles of reagent were as follows: (δ,CCl_4): 1.19 (s,3H); 1.30 (d, J = 7 Hz, 3H); 1.41 (s,3H); 1.53 (d, J = 7 Hz, 3H). As more shift reagent was added the signals began to coalesce and could not be differentiated.

An attempt to differentiate enantiomers by ^{1}H-NMR was also made using tris- [3-(trifluoromethylhydroxymethylene)-d-camphorato] (Aldrich, #17, 770-9). However, the peaks in the ^{1}H-NMR spectrum began to coalesce with the first addition (0.03 mmole) of the shift reagent.

Time Study of Formolysis of Carotol at 45°C

Carotol (1) (10-12 mg) was stirred at 45°C. Then 90% formic acid (1.0 ml) was added. After stirring at 45°C for a

designated time (5 min to 144 hours) the reactions were quenched by placing the vials in ice and adding saturated salt solution (1.0 ml). The products were extracted with ether (2 x 1.0 ml). Aliquots were injected into the glc (Col I, 140°C) to determine the identity and amount of products. Products were identified by comparison of retention times as on Table 4 and mixed injections of standards. Product distribution was measured by peak areas of the glc (Col I, 140°C) tracings using corrections for variations of product response (Table 1). Table 5* contains the data for the distribution of major products for the first six hours of formolysis, while data for the major products formed from 24 to 144 hours appear in Table 6* and that for the complete time study including unknowns is in Table 7. A comparison of the percentages of tricyclodaucene (17) and isotricyclodaucene (18) (Col I, 100°C) produced from one to one hundred forty-four hours is in Table 8.*

*These tables are illustrated in Figures 8, 9, and 10 of the discussion.

Table 4. Retention Times* of Formolysis Products

Product	R_t (140°C)	R_t (160°C)
Olefins 17, 18	2 min 41 sec	1 min
Daucene (9)	3 min 5 sec	1 min 34 sec
Daucane Ether (19)	3 min 37 sec	1 min 36 sec
Acoradienes (16)	4 min 2 sec	---
Tricyclocarotol (20)	7 min 36 sec	3 min 12 sec
Tricyclocarotol formate (21)	13 min 17 sec	5 min 26 sec

*(Col I)

Table 5. Percentages of Major Products from Formolysis of Carotol During First Six Hours at 45°C

	Percent					
Hours	Daucene (9)	Acoradienes (16)	Olefins 17,18	Ether 19	Alcohol 20	Formate 21
0.25	83.8	12.9	2.7	0.0	0.8	0.8
0.5	57.6	11.4	5.5	6.8	3.0	15.7
1.0	46.4	11.5	10.1	6.3	3.7	22.0
2.0	20.8	10.1	13.1	8.7	6.6	40.7
3.0	9.6	2.6	19.5	9.2	9.1	50.0
4.0	4.2	0.0	13.7	11.5	14.6	56.0
6.0	4.5	0.0	18.6	14.7	16.0	46.2

Table 6. Percentages of Major Equilibrium Products from Formolysis of Carotol (1) for 24 to 144 Hours at 45°C

Hours	Olefins 17,18	Ether 19	Alcohol 20	Formate 21
24	37.7	22.8	19.7	15.4
48	41.4	19.1	25.1	14.4
72	42.4	23.4	22.3	11.9
96	54.1	16.9	13.4	15.6
144	80.4	11.8	1.6	6.2

Table 7. Percentages of All Products from Formolysis of Carotol at 45°C

Hours	Olefins 17,18	Daucene (9)	Acoradienes (16)	Ether 19	Alcohol 20	Formate 21	Unknowns
0.25	2.6	77.4	13.1	0.0	0.7	0.8	5.4
0.50	4.7	49.1	9.7	5.8	2.6	13.4	14.7
1.0	8.0	37.1	9.2	5.0	2.9	20.5	20.2
2.0	11.1	17.6	8.6	7.4	5.6	34.7	15.0
3.0	17.3	8.5	2.3	8.2	8.0	44.5	11.2
4.0	12.1	3,7	0.0	10,1	16.4	45,6	12.1
6.0	15.6	3.7	0.0	12.4	13.4	38.8	16.1
24	34.2	4.0	0.0	20.8	17.9	14.0	9.0
48	35.3	0.0	0.0	16,3	21.4	12,4	14.6
72	38.4	0.0	0.0	21.5	20.4	11.5	8.2
96	45.5	0.0	0.0	14.2	11.2	13.1	16.0
144	70.9	0.0	0.0	11.8	17.9	14.0	9.1

Table 8. Ratio of Trisubstituted 17 to Tetrasubstituted 18 Olefins from Formolysis of Carotol (1) at 45°C

Time (hours)	Tricyclodaucene (17)	Isotricyclodaucene (18)
1	100.0	0.00
4	83.0	17.0
24	78.0	22.0
72	30.0	70.0
96	24.0	76.0
144	11.0	89.0

Preparation of Tricyclocarotol-p-Iodobenzoate (22)

Tricyclocarotol (20) (1.1g, 5.2 mmoles) was dissolved in freshly distilled dimethoxyethane (4.0 ml) under a nitrogen atmosphere. Then, n-butyl lithium (3.5 ml, 1.5 M) was slowly added keeping the temperature around 25°C with an ice bath. After 20 minutes, p-iodobenzoylchloride (1.36g, 6.2 mmoles) in dimethoxyethane (2.0 ml) was added dropwise and stirring was continued at room temperature for 18 hours. This solution was diluted with ether (150 ml) and was successively washed with water (5x50 ml), saturated salt solution (3x50 ml), dried over magnesium sulfate, filtered and evaporated in vacuo to yield a yellow viscous oil (1.95g).

Purification of this product was effected by chromatography on silica gel (200g) eluting the ester 22 with hexane-benzene (1:1) followed by crystallization from pentane at dry ice-acetone temperature to give a white solid with one spot on tlc (ethyl acetate-petroleum ether, 1:9) and one peak on glc (R_t = 8 min 31 sec, Col II, 210°C). Large plate crystals for x-ray analysis were slowly obtained from ethyl acetate at 0°C and their spectral properties appear below:

mp 107-110°C

IR: ν_{nujol} (cm^{-1}): 1724, 1580, 1450, 1280, 1270, 1110 and 1100.

^{1}H-NMR (δ,$CDCl_3$): 0.87 (s,3H); 1.02 (s,3H); 1.07 (d, J = 6 Hz,3H); 1.10 (d, J = 6 Hz,3H); 7.75 (m,4H).

Mass spectrum: M^+ = 452 (<0.01%); m/e = 161 (100%).

Analysis ($C_{22}H_{29}O_2$): calculated: C 58.40, H 6.45

found: C 58.37, H 6.45.

Lithium Aluminum Hydride Reduction of Tricyclocarotol-p-iodobenzoate (22)

Tricyclocarotol-p-iodobenzoate (115 mg, 0.25 mmole) was dissolved in anhydrous ethyl ether (10 ml). After cooling the solution to 0°C, lithium aluminum hydride (95 mg, 2.5 mmoles) was added. Stirring was continued at room temperature for 2.5 hours. Excess lithium aluminum hydride was destroyed by adding small pieces of ice. When the gray color had disappeared, water (25 ml) was added and the solution was extracted with ethyl ether (3 x 20 ml). Then, the combined ether extracts were washed with water (3 x 20 ml), dried over magnesium sulfate filtered and evaporated *in vacuo* to yield a yellow oil (82.8 mg) which showed that tricyclocarotol was present by glc analysis (Col II, 150°C).

The product was chromatographed on silica gel (8.0g) to yield an alcohol (43 mg, 1:1 benzene-hexane eluent) which was identical by glc retention time with an authentic sample of tricyclocarotol (20) and had an identical ^{1}H-NMR to that previously reported.

Preparation of Tricyclocarotol-p-bromobenzoate

Tricyclocarotol (20) (44 mg, 0.2 mmole) was dissolved in freshly distilled ethyl ether (1.5 ml). Then n-butyl lithium in hexane (0.3 ml, 0.05 mmole) followed by p-bromobenzoyl chloride (227 mg, 0.92 mmole) was added. After stirring for 20 hours, water (10 ml) and 10% sodium hydroxide solution (10 ml) were added to the reactants. This basic solution was extracted with ether (3 x 20 ml); then, the combined ether extracts were washed neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated in vacuo to yield a semi-solid (212 mg) with the following spectrum:

IR: ν_{neat} (cm^{-1}): 3500, 1775, 1720, 1580, 1470, 1280, 1200, 1175, 1100.

In order to remove unreacted chloride and acid, the above product was stirred at room temperature with 10% sodium hydroxide solution for two hours. The organic product was then dissolved in ether and worked up as before to yield a yellow oil (163 mg). Its IR showed the disappearance of the bands at 3500 and 1775 (cm^{-1}).

Preparation of Tricyclocarotol-bromoacetate[26]

Tricyclocarotol (20) (60.9 mg, 0.27 mmole) was dissolved in dimethyl aniline (0.85 ml); the solution was cooled to 0°C and bromoacetyl bromide (0.06 ml, 0.78 mmole) was added. After ten minutes, the ice-bath was removed. At

the end of 1.25 hours, the sticky product was dissolved in ether (20 ml) to which water (30 ml) was added. After separating the layers, the water was extracted with ether (2 x 20 ml), the combined ether fractions were successively washed with 10% sulfuric acid solution (3 x 10 ml), saturated potassium bicarbonate solution (2 x 10 ml), water until neutral to litmus, dried over magnesium sulfate, filtered and evaporated in vacuo. The IR of the crude green oil (139 mg) is as follows: ν_{neat} (cm^{-1}): 1775 (br); 1725 (br).

The major portion (113 mg), a yellow oil, which was obtained from silica gel (10g) chromatography (benzene eluent) had the following ^{1}H-NMR:

(δ,$CDCl_3$): 0.97-2.27 (complex multiplet); 4.03 (m); 4.57 (s).

Preparation of Tricyclocarotol-benzoate Using Dimethylaniline

Tricyclocarotol (60g, 0.27 mmole) was dissolved in freshly distilled dimethylaniline (1.0 ml). Then, freshly prepared benzoyl chloride (0.1 ml, 121 mg, 0.87 mmoles) was added. After stirring for two hours at room temperature, the blue solution was poured into ice water. When the ice had dissolved, the aqueous solution was extracted with ether (3 x 20 ml), the combined ether fractions were washed successively with 10% sulfuric acid solution, saturated potassium bicarbonate solution and then neutral to litmus with water. After drying with magnesium sulfate and filtering, the product was evaporated in vacuo to give a yellow oil with

the following characteristic IR absorptions: ν_{neat} (cm^{-1}): 3450, 1780, 1725, 1600, 1500, 1200 and 1175.

Since there was unreacted hydroxyl, the product was redissolved in dimethylaniline (1.0 ml) and benzoyl chloride (0.1 ml) was added as above. Stirring was continued at room temperature for four hours and the above work-up repeated to yield a yellow oil with an IR identical to that above with the following NMR:

$\delta(CDCl_3)$: 0.85 (s); 0.93 (s); 1.02 (d, J = 6 Hz); 1.15 (d, J = 6 Hz); 1.22-1.78 (complex multiplet); 7.35 (complex multiplet); 8.17 (complex multiplet).

Preparation of Tricyclocarotolbenzoate using n-Butyl Lithium[25]

After adding n-butyl lithium in hexane (0.3 ml, 0.54 mmole) to a solution of tricyclocarotol (20) (45.6 mg, 0.21 mmole) in anhydrous ethyl ether, benzoylchloride (0.1 ml, 0.87 mmole) was added. This solution was diluted with ether after stirring at room temperature for 19 hours. It was then washed with 10% sodium hydroxide solution, then neutral to litmus with water, dried over magnesium sulfate and concentrated *in vacuo* to give a yellow oil with the following spectra:

IR: ν_{neat} (cm^{-1}): 1780, 1725, 1600, 1680, 1450, 1175 and 1120.

^{2}H-NMR (δ,$CDCl_3$): 0.82-1.72 (complex multiplet); 4.33 (t); 7.37 and 8.02 (complex multiplets).

Chromatography on silica gel (10g) gave one fraction (48 mg, 1:1 benzene-hexane eluent). The spectral properties of this oil were as follows:

IR: ν_{neat} (cm^{-1}): 1725, 1580, 1450, 1280, 1100, 1025, and 700.

^{1}H-NMR (δ,$CDCl_3$): 0.88 (s,3H), 1.00 (s,3H), 1.08 (d, J = 6 Hz,3H), 1.10 (d, J = 6 Hz,3H), 7.37 and 8.02 (complex multiplets).

The second fraction (69 mg, benzene eluent) had a similar IR to the unchromatographed oil but its proton NMR was different.

$\delta(CDCl_3)$: 0.83-1.73 (complex multiplet); 4.30 (tr); 7.37 and 8.02 (complex multiplets).

Lithium Aluminum Hydride Reduction of Tricyclocarotolbenzoate

Lithium aluminum hydride (125 mg, 3.3 mmole) was added to a solution of tricyclocarotolbenzoate (47.8 mg, 0.15 mmole) in anhydrous ether cooled to 0°C. After stirring at room temperature for two hours, the reaction was quenched by adding ice chips and then worked up as described previously for other hydride reductions to yield an oil. Glc analysis (Col. I, 170°C) showed a mixture that was predominantly tricyclocarotol (20). Its NMR spectrum was identical to that previously described.

Attempted Preparation of Tricyclocarotol-β-Bromopropionyl Isocyanate[27]

Allyl chloride (0.3 ml) and a trace of benzoyl peroxide were added to a solution of n-bromosuccinimide (300 mg, 1.69 mmole) in dry carbon tetrachloride. After refluxing for thirty minutes, the solution was cooled to room temperature and tricyclocarotol (20) in chloroform (1.0 ml) was added to it. Stirring was continued for 10 minutes and the solvent was removed in vacuo. Then, the solid product was dissolved in ether which was washed with water (2x20 ml), dried over magnesium sulfate, filtered and evaporated in vacuo. Dissolution in methanol yielded fine

white crystals which were filtered and identified as benzoyl peroxide mp 105-106°C (lit mp 105)[28] by ^{1}H-NMR; while the glc (Col I, 160°C) of the supernatant showed a complex mixture.

Preparation of Tricyclodaucene Diol (23)[29]

Aqueous sodium bisulfite (3.0g in 3.0 ml) was added to a solution containing tricyclodancene (17) (199 mg, 0.9 mmole) and osmium tetroxide (250 mg, 0.9 mmole) in pyridine (5.0 ml) that had been stirring for 7 days in the dark. After all of the orange solid had dissolved, water (10 ml) was added and this solution was extracted with methylene chloride (3x15 ml). Then, the combined methylene chloride extracts were washed with saturated salt solution (3x10 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a brown oil (217 mg).

This product was chromatographed on activity III, neutral alumina (20g) eluting a brownish solid (193 mg) with ether-benzene (1:5) that had strong absorption in the IR at 3400 cm^{-1}. After chromatographing the solid again, white needles (mp 85-87°C) with one peak on GC (Col I, 160°C) were obtained by crystallization from pentane. One of these was used for x-ray analysis. The observed spectral properties of 23 were:

IR: ν_{neat} (cm^{-1}): 3400, 1470, 1375, 1050.

^{1}H-NMR (δ,$CDCl_3$): 0.83 (d, J = 6 Hz, 3H); 0.90 (d, J =

6 Hz, 3H); 1.00 (s,3H); 1.33 (s,3H); 3.82 (t, J = 7 Hz, 1H).
Mass spectrum: M^+ (none); m/e = 123 (100%).
ORD (c = 1.00, $CHCl_3$): $[\phi]_{650}$ = 23.8°, $[\phi]_{589}$ = 33.3° ($[\alpha]_{589}$ = 14.0°), $[\phi]_{550}$ = 38.1°, $[\phi]_{450}$ = 66.6°, $[\phi]_{350}$ = 143°.
Analysis ($C_{15}H_{26}O_2$): Calculated: C, 75.63; H, 10.92.
Found: C, 75.41; H, 10.96.

Epoxidation of Tricyclodaucene (17) and Isotricyclodaucene (18) Mixture in a Biphasic System[30]

Solid m-chloroperbenzoic acid (863 mg, 5.0 mmoles) was slowly added to a stirred solution of a mixture (505 mg) of tricyclodaucene (17) (1.8 mmole) and isotricyclodaucene (18) (0.69 mmole) in a biphasic system containing methylene chloride (10 ml) and 0.5 M aqueous sodium bicarbonate solution (15 ml). After stirring at room temperature for 17 hours, the solution still gave a positive starch iodide test. The methylene chloride layer was separated, washed with 1 N sodium hydroxide solution (20 ml), then neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a colorless oil (553 mg). Glc analysis (Col I, 140°C) showed one narrow peak (R_t = 2 min 57 sec) and one broad peak (R_t = 3 min 40 sec).

The epoxide mixture was chromatographed on activity III, neutral alumina (55.0g). The first fraction (254 mg, hexane eluent) contained the epoxide 24, (R_t = 3 min 40 sec), which corresponded to the product from tricyclodaucene (17),

while the second fraction (107 mg, hexane eluent) contained the epoxide 26 (R_t = 2 min 57 sec) which was the product from isotricyclodaucene 18.

The spectral and physical properties of the epoxides are as follows:

Isotricyclodaucene epoxide (26)

bp 80°C/0.3 mm (hot box).

IR: ν_{neat} (cm^{-1}): 1150, 1110, 850.

^{1}H-NMR (δ,$CDCl_3$): 0.93 (s,3H); 1.05 (s,3H); 1.32 (s,3H); 1.36 (s,3H).

^{13}C-NMR (δ,$CDCl_3$): 77.2, 61.6 (epoxide carbons); 47.6 39.9 (quartenary carbons); 45.9, 44.5, 42.2, 41.7, 35.7, 32.3, 31.7, 26.1, 23.2, 20.9, 18.9.

Mass spectrum: M^+ = 220 (5%), m/e = 177 (100%).

ORD (c = 2.17, $CHCl_3$): $[\phi]_{650}$ = 31.4°, $[\phi]_{589}$ = 37.7° ($[\alpha]_{589}$ = 83.0°), $[\phi]_{500}$ = 52.4°, $[\phi]_{400}$ = 79.6°, $[\phi]_{300}$ = 152.9°.

Analysis ($C_{15}H_{24}O$): calculated: C, 81.76; H, 10.98.
Found: C, 81.71; H, 11.14.

Tricyclodaucene Epoxide (24)

IR: ν_{neat} (cm^{-1}): 1720, 1210, 1060, 890 and 850.

^{1}H-NMR (δ,$CDCl_3$): 0.90 (d, J = 6 Hz, 6H); 0.95 (s,3H); 1.32 (s,3H); 2.90 (m,1H).

^{13}C-NMR (δ,$CDCl_3$): 25 signals including 212.3 (C=O); 153.3 (trisubstituted epoxide carbon); 110.8 (disubstituted epoxide carbon).

Mass Spectrum: M^+ = 220 (14%), m/e = 28 (100%).

Epoxidation of Tricyclodaucene (17) in a Biphasic System[30]

Solid m-chloroperbenzoic acid (72.1 mg, 0.40 mmole) was added to a stirred biphasic system of methylene chloride (3.0 ml) and 0.5 M aqueous sodium bicarbonate solution (1.0 ml) containing tricyclodaucene (17) (51.4 mg, 0.25 mmole) over a period of 2 hours. After 20 hours, glc analysis (Col. III, 140°C) showed the presence of some starting olefin (R_t = 33 sec), a major peak (R_t = 1 min 7 sec) and a minor peak (R_t = 2 min), while the solution was negative to starch iodide paper. Additional per acid (14.0 mg, 0.08 mmole) was added. After 30 min, glc showed the absence of olefin 17. The work up was repeated as above for the epoxidation of the olefin mixture to yield an oil (45.1 mg). Glc analysis (Col. III, 140°C) showed one major peak (R_t = 1 min 7 sec) and a minor peak (R_t = 2 min).

The IR and ^{1}H-NMR was the same as that previously reported for the epoxide of tricyclodaucene (24).

Rearrangement of Epoxide of Tricyclodaucene (24) on Activity I, Neutral Alumina

In order to remove the minor impurity from the biphasic epoxidation of 17, the epoxide product 24 (45 mg) was

chromatographed on activity I, neutral alumina (5.0g). Nothing was eluted with hexane or benzene. However, an oil (33 mg) was finally eluted with 10% ether-benzene. Glc analysis (Col. III, 120°C) showed two major peaks with short retention times (R_t = 58 sec, R_t = 1 min 75 sec) and a major one with longer retention time (R_t = 5 min 17 sec).

The spectral properties of the mixture are shown below.

IR: ν_{neat} (cm^{-1}): 1710, 1680, 1610.

^{1}H-NMR (δ,$CDCl_3$): 0.90 (d, J = 6 Hz, 3H); 0.93 (d, J = 6 Hz, 3H); 0.98 (s,3H); 1.01 (d, J = 6 Hz, 3H). (Shoulders were present on these above signals) 2.33 (d, J = 3 Hz, 1H), 6.03 (s, 0.5 H).

Epoxidation of Isotricyclodaucene (18) in a Biphasic System[30]

Isotricyclodaucene (18) (83 mg, 0.41 mmole) was treated with m-chloroperbenzoic acid (70.9 mg, 0.41 mmole) in a biphasic system of methylene chloride (3.0 ml) and 0.5 M sodium bicarbonate solution (1.0 ml) and after 24 hours worked up as above in the epoxidation of the olefin mixture. The solution was negative to starch iodide paper.

Glc (Col I, 170°C) showed one peak (R_t = 2 min). The spectral properties for the epoxide 26 appear above.

Rearrangement of Epoxide of Isotricyclodancene 26 on Activity I, Neutral Alumina

The tetra substituted epoxide 26 (51 mg) was chromatographed on activity I, neutral alumina (5.0g). Nothing was eluted with hexane or benzene, however an oil (57 mg) was eluted with ether-benzene (1:9). Glc analysis of the eluent (Col III, 125°C) showed three minor peaks (R_t = 38 sec, 43 sec, 53 sec) and one major peak (R_t = 3 min 7 sec). Distinctive spectral properties of the mixture are shown below:

IR: ν_{neat} (cm^{-1}): 1700, 1620.

^{1}H-NMR (δ,$CDCl_3$): 0.85-1.02 (complex multiplet); 1.12 (s,3H), 2.11 (s,3H), 6.03 (s,1H).

Epoxidation of Tricyclodancene (17) in a Homogeneous Solution[31]

After cooling a stirred solution of olefin (98 mg, 0.48 mmole) in methylene chloride to 0°C, m-chloroperbenzoic acid was added over a 2 hour period. At this time glc analysis (Col II, 150°C) showed two major peaks (R_t = 1 min 54 sec, 2 min 30 sec) and one minor peak (R_t = 1 min 15 sec). Saturated sodium bisulfite solution (5.0 ml) and more methylene chloride were added. The layers were separated and the methylene chloride was washed successively with saturated bisulfite solution (20 ml), saturated bicarbonate solution (20 ml), saturated salt solution (20 ml), dried over magnesium sulfate filtered and evaporated in vacuo to yield a white

semi-solid (112 mg). Analysis by glc (Col II, 125°C) showed that one component, the ketone 25, was present which had the following spectral properties:

IR: ν_{neat} (cm^{-1}): 1710, 1460, 1375.

^{1}H-NMR (δ,$CDCl_3$): 0.90 (d, J = 6 Hz, 3H); 0.93 (d, J = 6 Hz, 3H); 0.98 (s,3H); 1.01 (d, J = 6 Hz, 3H); 2.33 (d, J = 3 Hz, 1H).

Mass spectrum: M^+ = 220 (65%), m/e 123 (100%).

Experimental exact mass = 220.188 ± 0.004, calculated ($C_{15}H_{24}O$) = 220.183.

Preparation of the 2,4-Dinitrophenylhydrazone of Ketone 25[32]

A solution (5.0 ml) of ethanolic hydrochloric acid (0.5 ml HCl / 25 ml ethanol) was added to the ketone 25 (52 mg, 0.24 mmole). After heating on the steam-bath for ten minutes and cooling to room temperature, a solid formed. This was filtered to give an orange solid (70 mg, mp 115-117°C) which showed one spot on tlc (R_t = 0.7, benzene). Orange flake crystals were obtained from methanol for analysis. While larger crystals for x-ray analysis were obtained by dissolving the solid in chloroform containing a small amount of isopropanol and keeping the solution in an isopropanol saturated atmosphere. Attempts to determine the structure by x-ray failed as the crystals were twinned.

Spectral properties of the 2,4-dinitrophenylhydrazone were:

mp 115-117°C

IR: ν_{CCl_4} (cm^{-1}): 3340, 1700, 1600, 1570, 1520.

^{1}H-NMR (δ,$CDCl_3$): 0.94 (s,3H), 0.95 (d, J = 6 Hz, 3H); 0.98 (d, J = 6 Hz, 3H); 0.99 (d, J = 6 Hz, 3H); 8.03 (m,3H); 11.02 (s,1H).

Mass spectrum: M^+ = 400 (81%), m/e = 149 (100%).

Analysis ($C_{21}H_{28}O_4N_4$): calculated: C, 62.98; H, 7.05.
Found: C, 63.01; H, 7.08.

Reduction of Ketone 25

The ketone 25 (58 mg, 0.26 mmole) was dissolved in anhydrous ether. The stirred solution was cooled in an ice-bath while lithium aluminum hydride (100 mg, 2.6 mmoles) was added. After stirring at room temperature for three days, chips of ice were slowly added and stirring continued until the gray color disappeared. The mixture was diluted with water and extracted with ether (3x20 ml). The combined ether fractions were washed with water (3x20 ml), dried over magnesium sulfate, filtered and evaporated in vacuo. Glc analysis (Col I, 170°C) showed one peak (R_t = 2 min 48 sec). There was a strong absorbance at 3400 cm^{-1} (hydroxyl group) and absence of carbonyl absorption in the infrared spectrum. While the following signals were observed in the ^{1}H-NMR (δ,$CDCl_3$) spectrum: 0.88 (d, J = 6 Hz, 3H); 0.92 (d, J = 6 Hz, 3H); 1.10 (d, J = 6 Hz, 3H); 1.10 (s,3H); 3.81 (s,1H).

Reaction of Tricyclodaucene Epoxide (24) Mixture with Lithium Aluminum Hydride

The product (158 mg, 0.71 mmole) from the tricyclodaucene epoxidation was stirred in freshly distilled THF (10 ml) at room temperature. An excess of lithium aluminum hydride (750 mg, 19.5 mmoles) was added to the above during the course of four days. The reaction was followed by glc (Col. I, 160°C). There was basically no change in the glc after 1 day or three days. The reactants were heated to 55°C for four more days. After seven days total reaction time there were two major peaks by glc (R_t = 2 min 38 sec, 3 min 36 sec) and several minor ones. The reaction was quenched by stirring with an excess of saturated sodium potassium tartrate solution. Then ether (20 ml) was added. After separating the layers, the aqueous layer was extracted with ether (2x20 ml). The combined ether fractions were washed neutral to litmus with water dried over magnesium sulfate, filtered and evaporated in vacuo to yield a colorless oil (111 mg).

This product was chromatographed on basic alumina. The first fraction (44 mg) was identified as epoxide 24 according to its IR and ^{1}H-NMR spectra, while the second fraction (55 mg) showed strong absorption at 3400 cm^{-1} in its IR spectrum. The ^{1}H-NMR (δ,$CDCl_3$) contained the following signals: 0.83 (d, J = 6 Hz, 3H); 0.87 (d, J = 6 Hz, 3H); 1.02 (d, J = 6 Hz, 3H); 1.10 (s,3H); 3.83 (s,1H).

Ozonolysis of Tricyclodaucene (17)--Reductive Work-up[33]

A gas solution of ozone in oxygen (4%) was bubbled through methylene chloride (30 ml) containing the olefin 17 (125 mg, 0.61 mmole) at -70°C for ten minutes after the solution had turned blue. Then the solution was brought to 0°C in an ice-bath and zinc dust (372 mg) in 75% acetic acid (10 ml) was added. After stirring at room temperature for 24 hours, the solids were removed by filtration and the solution was made basic to litmus with 10% sodium hydroxide. After extracting this solution with methylene chloride (4x25 ml) the combined extracts were washed until neutral to litmus, dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a yellow oil (97 mg) which had one major peak by glc (R_t = 1 min 21 sec, Col IV, 145°C) along with three minor ones and the following IR and ^{1}H-NMR spectra:

IR: ν_{neat} (cm^{-1}): 3450 (w), 1710, 1720 and 1740 (sh).

^{1}H-NMR: looks like spectrum from ketone 25 with some impurities.

Ozonolysis of Tricyclodaucene (17)--Oxidative Work-up[34]

The olefin 17 (94.4 mg, 0.46 mmoles) was ozonized as above. Then, 5% potassium bicarbonate solution (15 ml) was added followed by 30% hydrogen peroxide (10 ml) and the solution was stirred at room temperature for 20 hours.

Sodium bisulfate (solid) was added, until bubbling stopped.

The solution was transferred to a separatory funnel and extracted with ether (3x20 ml). Then the ether fractions were combined, washed until neutral to litmus with water, dried over magnesium sulfate and evaporated *in vacuo* to give a yellow oil. Since there was broad acid absorbance in the IR, the oil was dissolved in ether which was then washed with 10% sodium hydroxide solution (3x15 ml), then washed until neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated *in vacuo* to give a yellow oil (40.3 mg). Analysis by glc (Col IV, 160°C) showed one major peak (95%, R_t = 37 sec). The IR and ^{1}H-NMR were the same as for ketone 25.

An acid fraction was obtained by acidifying the combined basic washings from above. This was extracted with ether (3x20 ml), and the combined ether fractions were washed until neutral to litmus, dried over magnesium sulfate, filtered and evaporated *in vacuo* to give a yellowish oil (9.0 mg). The IR showed that an acid was present while the ^{1}H-NMR consisted of indiscernable highfield multiplets.

Oxidation of Tricyclodaucene (17) with Sodium Metaperiodate and Potassium Permanganate[8]

The olefin 17 (31 mg, 0.15 mmoles) was dissolved in distilled tertiary butanol (16 ml). Then a solution of sodium metaperiodate (0.25 g, 1.2 mmoles), potassium permanganate

(0.007g, 0.05 mmole) and potassium carbonate (0.043g, 0.45 mmole) in water (17 ml) was added to it while stirring at room temperature. After 18 hours, water (30 ml) was added, the solution extracted with benzene (3x20 ml) and the combined organic fractions were washed with water (3x20 ml), dried over magnesium sulfate, filtered and evaporated in vacuo to give a yellow oil (39.2 mg). Glc (Col IV, 165°C) showed three new peaks in addition to a small amount of starting olefin and the IR showed that an acid was present.

A 10% sodium hydroxide solution (10 ml) was added to the above product and this was extracted with benzene (3x15 ml) to give a neutral fraction. The combined benzene extracts were washed until neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated in vacuo to give a yellow semi-solid (26.8 mg). The infrared spectrum showed a small absorbance at 3450 cm^{-1} for a hydroxyl group and a broad absorbance at 1720 cm^{-1} for carbonyl groups, while the ^{1}H-NMR spectrum was complex.

The acidic fraction which obtained by acidification and extraction of the aqueous solution with benzene as described above for the neutral fraction to ultimately give a yellow oil (9.5 mg). There were absorbancies at 3000 and 1710 cm^{-1} in the infrared and the ^{1}H-NMR spectrum was complex.

Preparation of Hydrazone Derivatives of Ketone 18

5-Iodo-2-nitrophenylhydrazine Preparation[35]

The 1,2-dinitro-4-iodobenzene (500 mg, 1.7 mmole), prepared by McClure,[35] was dissolved in absolute ethanol to give a yellow solution. This was cooled to 0°C while stirring and a 64% hydrazine hydrate solution (0.1 ml, 2 mmole) was added. Stirring was continued at 0°C for 60 minutes at which time the solution was dark orange with some organge solid. The ethanol was concentrated to 3 ml *in vacuo* to give a reddish solid (185 mg) and crystallization from methanol gave shiney orange plate crystals (66 mg), mp 147-150°C (lit. 150°C).[36] Another crop (83 mg) was also obtained from methanol.

IR: ν_{nujol} (cm^{-1}) = 3310.

^{1}H-NMR (δ,$CDCl_3$): 3.82 (m,3H); 7.05 (d, d, J_1 = 9 Hz, J_2 = 2 Hz, 1H); 7.81 (d, J = 9 Hz, 1H); 8.13 (d, J = 2 Hz, 1H).

Preparation of 5-iodo-2-nitrophenylhydrazone of Ketone 18

The 5-iodo-2-nitrophenylhydrazine (141 mg, 0.51 mmole) was dissolved in 95% EtOH (10 ml) which contained 2 drops of sulfuric acid. After warming on the steam-bath, this solution was added to the ketone 18 (104 mg, 0.48 mmole) and heating was continued for 2 mintues. Upon cooling, an orange solid came out of solution. Upon filtration it was shown

to be mostly unreacted hydrazine by tlc (R_f = 0, hexane-benzene, 3:2); while the supernatant contained hydrazone (R_f = 0.5) plus unreacted hydrazine. This supernatant solution was concentrated and applied to a neutral alumina column (5g) in hexane.

Pure hydrazone (50 mg), (one spot R_f = 0.5, tlc as above) was eluted with 10% ether in benzene. It had the following spectra:

^{1}H-NMR (δ,$CDCl_3$): 0.90 (d, J = 6 Hz, 3H); 0.92 (d, J = 6 Hz, 3H); 0.97 (d, J = 6 Hz, 3H); 0.97 (s,3H); 2.35 (d, J = 4 Hz, 1H); 7.3 (m,2H); 8.08 (d, d, J_1 = 24 Hz, J_2 = 2 Hz, 1H).

Preparation of Isotricyclodaucene Diol (27)[29]

A solution of the tetra-substituted olefin 18 (185 mg, 0.9 mmole) and osmium tetroxide (250 mg, 0.9 mmole) in dry pyridine (5.0 ml) was stirred in the dark for 7 days. Then aqueous sodium bisulfite solution (1.0g/3.0 ml) was added and stirring was continued for 45 minutes. More water (10 ml) was added and the solution was extracted with methylene chloride (3x20 ml) which were combined and washed with saturated salt solution (3x10 ml), then evaporated in vacuo to give a dark brown oil. Analysis by glc (Col I, 160°C) showed one peak (R_t = 2 min 53 sec).

The crude product from a second osmylation was combined with the above and this product (425 mg) was

chromatographed on activity III, neutral alumina (40g) to give a slightly purple solid (340 mg, benzene eluent). Attempts to obtain a crystal for x-ray analysis resulted in a white powder (mp 86-88°C) from pentane and then colorless needles (mp 68-69°C), also from pentane. Although both solids had the same spectral properties (IR, NMR and glc) their analyses after drying at 25°C/0.3 mm were different and did not correspond to the theoretical values. These results appear below.

A crystal was mounted on the diffractometer, but decomposition was noted by a decrease of more than 8% in the integrated intensities of the test reflections after the first cycle of data collection or 17 hours. Coating a second crystal with epoxy did not alter the decomposition.

IR: ν_{neat} (cm^{-1}): 3500, 1175.

^{1}H-NMR (δ,$CDCl_3$): 0.89 (s,3H); 1.07 (s,3H); 1.20 (s,3H); 1.26 (s,3H).

Mass spectrum: M^+ not found calculated ($C_{15}H_{26}O_2$) = 238; m/e 177 (100%).

Analysis ($C_{15}H_{26}O_2$): Calculated: C, 75.88; H, 10.99.

Found (mp 86-88°C): C, 73.86; H, 10.62.*

C, 73.94; H, 10.58.

(mp 68-69°C): C, 76.64; H, 11.05.**

C, 76.71; H, 11.05.

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*1/2 mole water plus 1 mole diol: Calculated: C, 72.87; H, 10.93.

**1/2 mole pentane plus 1 mole diol: Calculated: C, 76.92; H, 11.36.

Preparation of Tricyclopentanone 28 from Isotricyclodaucene (18) and Lead Tetraacetate[37]

The diol 27 from isotricyclodaucene (18) (156 mg, 0.66 mmole) was dissolved in dry benzene (40 ml) and cooled in an ice-bath under nitrogen. Then lead tetraacetate (327 mg, 0.74 mmole) in dry benzene (20 ml) was added over a 15 minute period. Stirring was continued for 1-1/2 hours in the cold and the brown solid which had formed was removed by filtration through Cellite. After evaporating the benzene in vacuo, ether (50 ml) was added and washed with saturated potassium bicarbonate solution (3x10 ml), neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated in vacuo to yield a brown oil (112 mg). Glc analysis (Col. I, 140°C) showed that 68% of the diol 28 had disappeared. Chromatography on activity III, neutral alumina (10g) gave one fraction (51.4 mg, 25% benzene-hexane eluent) which had one peak by glc analysis (Col I, 140°, R_t = 1 min 24 sec) that corresponded to the tricyclic ketone 28 with the spectral properties that appear below and a second fraction (30 mg, 100% benzene eluent) that contained the starting diol 27 with the ^{1}H-NMR as reported above.

IR: ν_{neat} (cm^{-1}): 1745 (cyclopentanone); 1460, 1375 (CH_3-C-); 1175, 1100 (ketone).

^{1}H-NMR: 0.97 (s,3H); 1.05 (s,3H); 1.98 (br,1H); 2.46 (br,1H).

^{13}C-NMR (δ,$CDCl_3$): 217.2 (C=O); 51.5 (H-C-C=O); 47.3 (H-C-C=O);

42.3 (q); 35.8 (q); 44.0, 40.7, 34.3, 31.6, 25.8, 18.8.

Mass spectrum: M^+ = 178 (66%), m/e = 107 (100%).

Experimental exact mass: 178.132 ± 0.004, calculated exact mass: 178.135 ($C_{12}H_{18}O$).

The analysis of the 2,4-dinitrophenylhydrazone, semicarbazone and p-bromosulfonylhydrazone which follow agree with the theoretical value.

Preparation of 2,4-Dinitrophenylhydrazone Derivative of Tricyclopentanone 28[32]

The pentanone 28 (51 mg, 0.29 mmole) was dissolved in hot ethanol (25 ml) containing hydrochloric acid (0.5 ml) and 2,4-dinitrophenylhydrazine (57 mg, 0.29 mmoles) and this solution was heated on the steam-bath for 20 minutes. Then, a portion of the ethanol (15 ml) was removed in vacuo. Upon cooling in an ice-bath the solid which had formed was removed by filtration to yield a light orange powder (46 mg) which had one spot by tlc (R_f = 1.0, benzene); while the supernatant liquid showed two spots (R_f = 0.0, 1.0). Crystallization from ethanolic chloroform gave orange needles which had the spectral properties below.

A crystal was mounted on the diffractometer for the x-ray determination of its structure. After obtaining values for a unit cell, an attempt was made to collect data. However the instrument could not recenter on the test reflections during the first cycle of data collection.

The following are the spectral and physical properties of the hydrazone:

mp 218-219°C

IR: ν_{CHCl_3} (cm^{-1}): 3320, 3100, 2010, 1625, 1600, 1510, 1450, 1520, 1345.

^{1}H-NMR (δ,$CDCl_3$): 0.97 (s,3H); 1.10 (s,3H); 2.57 (s,1H); 2.80 (s,1H); 7.84 (d, J = 10 Hz, 1H); 8.20 (d,d; J = 10 Hz, J_2 = 3 Hz; 1H); 9.15 (d, J = 3 Hz, 1H); 11.04 (s,1H).

Mass Spectrum: M^+ = 358 (63%); m/e = 107 (100%).

Analysis ($C_{18}H_{22}N_4O_4$): Calculated: C, 60.34; H, 6.19.
Found: C, 60.33; H, 6.21.

Oxidation of Isotricyclodaucene (18) with Sodium Metaperiodate and Potassium Permanganate[31]

After dissolving the olefin 18 (32.6 mg, 0.15 mmole) in tertiary butanol (16 ml), a solution of sodium metaperiodate (0.25g, 1.2 mmole), potassium permanganate (7.0 mg, 0.05 mmole) and potassium carbonate (43 mg, 0.45 mmole) in water (17 ml) was added to it. Stirring was continued at room temperature for 18 hours, then water (30 ml) was added and the solution was extracted with benzene (3x20 ml).

The combined benzene fractions were washed with water, dried over magnesium sulfate, filtered and evaporated in vacuo to give a yellow oil (19 mg) which had one major peak and four minor peaks by glc analysis (Col IV, 165°C). Its

infrared spectrum showed a broad hydroxyl peak at 3450 cm^{-1} and a broad carbonyl peak between 1745 and 1700 cm^{-1}; while the ^{1}H-NMR spectrum was complex.

Ozonolysis of Isotricyclodaucene (18)--Reductive Work-up

The olefin 18 (622 mg, 3.0 mmoles) was dissolved in ethyl acetate (10 ml). After cooling to 0°C, an ozone solution in oxygen was bubbled through the solution for 10 minutes. The solution was then warmed to room temperature and Zn dust (250 mg) in 75% glacial acetic acid (5.0 ml) was added. Stirring was continued under a nitrogen atmosphere for 1.5 hours. Then the solid which remained was removed by filtration and saturated potassium bicarbonate solution was added until the solution was basic to litmus. More ethyl acetate (25 ml) was added plus saturated salt solution (20 ml). The layers were separated and the ethyl acetate layer was washed with water until neutral to litmus, dried over magnesium sulfate, filtered and evaporated in vacuo to yield a viscous oil (627 mg) which showed one major product (~95%, R_t = 1 min 24 sec) by glc (Col I, 145°C). The non-volatile components were separated by chromatography on activity III, neutral alumina (60g) to give the pure tricyclopentanone 28 (190 mg) in the benzene hexane eluent (1:3). The spectra were identical with those from the product obtained from the lead tetraacetate oxidation of the tricyclic diol 27.

Baeyer-Villager Oxidation of the Tricyclopentanone 28[38]

The tricyclopentanone 28 (376 mg, 1.9 mmole) was dissolved in chloroform (5.0 ml); then solid m-chloroperbenzoic acid (400 mg, 2.2 mmoles) was added to this solution. After 24 hours of stirring in the dark, the reactants were diluted with chloroform (25 ml); and this solution was washed with saturated potassium bicarbonate solution (3x20 ml), with water until neutral to litmus and finally dried over magnesium sulfate, filtered and evaporated in vacuo to yield the tricyclolactone 30 (411 mg). Glc analysis (Col I, 160°) showed one major product (~95% pure, R_t = 5 min 36 sec) which gave white flakes after crystallization from ether-pentane. The physical and spectral properties appear below.

mp 63-64°C

IR: ν_{CHCl_3} (cm^{-1}): 1750, 1470, 1390, 1250, 1140 and 1050.

^{1}H-NMR (δ,$CDCl_3$): 0.98 (s,3H); 1.09 (s,3H); 2.78 (tr,d,$J_1$4.8, $J_2$1.7 Hz, 1H); 4.42 (tr,J,1.7 Hz, 1H).

Mass spectrum: M^+ = none, m/e = 107 (100%).

Analysis ($C_{12}H_{18}O_2$): Calculated: C, 74.19; H, 9.34.
Found: C, 74.31; H, 9.18.

Preparation of the Semicarbazone of 28[39]

The tricyclic pentanone 28 (48 mg, 0.27 mmole) was dissolved in methanol (0.5 ml) to which a solution containing sodium acetate (75 mg, 0.91 mmole) and semicarbazide hydrochloride (50 mg, 0.45 mmole) in water (0.5 ml) was

added. More methanol was added dropwise until the turbidity cleared. When no cyrstals appeared after 30 minutes, the solution was heated on the steam-bath for 5 minutes; then the reactants were allowed to stand at room temperature for 17 hours. The white solid which appeared was removed by filtration and recrystallized from benzene to give a white flocular solid. Attempts to obtain a crystal suitable for x-ray analysis failed. The physical and spectral properties of the semicarbazone appear below.

mp 205-207°C

IR: ν_{CHCl_3} (cm^{-1}): 3510, 2400, 1680, 1520.

^{1}H-NMR (δ,$CDCl_3$): 0.91 (s,3H); 1.03 (s,3H); 5.67 (s,2H); 7.83 (s,1H); 8.33 (s,1H).

Mass spectrum: M^+ = 235 (11%), m/e = 107 (100%).

Analysis ($C_{13}H_{21}ON_3$): Calculated: C, 66.38; H, 8.94.
Found: C, 66.37; H, 9.02.

Preparation of the p-Iodobenzoylhydrazone of 28[35]

The ketone 28 (53 mg, 0.30 mmole) was dissolved in a methanolic-water (4:1) solution (5.0 ml). After adding two drops of glacial acetic acid, p-iodobenzoylhydrazide (78 mg, 0.30 mmole) was added. The solution was heated on the steam-bath for 15 minutes and then allowed to stand at room temperature for 17 hours. The white solid precipitate was removed by filtration and recrystallized from acetonitrile. All attempts to obtain a crystal suitable for x-ray analysis resulted in an unsuitable white feathery solid. The following

are the physical and spectral properties of the derivative:

mp 204-206°C

IR: ν_{CHCl_3} (cm^{-1}): 3400, 1680, 1640, 1600, 1510, 1140, 1120, 1020, 920, 1480, 1270 and 1250.

^{1}H-NMR (δ,$CDCl_3$): 0.92 (s,3H); 1.05 (s,3H); 4.51 (m,1H); 4.73 (m,1H); 7.48 (d, J = 8 Hz, 2H); 7.75 (d, J = 8 Hz, 2H); 8.67 (s,1H).

Mass spectrum: M^+ = 422 (21%), m/e = 231 (100%).

Analysis ($C_{19}H_{23}ON_2I$): Calculated: C, 54.03; H, 5.45.
Found: C, 53.96; H, 5.53.

Preparation of the p-Bromosulfonylhydrazone of 28[36]

A solution of p-bromosulfonylhydrazide (70 mg, 0.30 mmole) in methanol (5.0 ml) containing one drop of glacial acetic acid was added to the tricyclic ketone 28 (67 mg, 0.30 mmole) dissolved in methanol (5.0 ml). After standing at room temperature for 30 minutes, the reactants were heated on the steam-bath for 5 minutes. A hard white solid was obtained after 17 hours at room temperature. This derivative was recrystallized from 95% ethanol-benzene. However, in an attempt at x-ray analysis failed as the crystal was twinned. Suitable crystals were not obtained from any solvent system. The spectral and physical properties appear below.

mp 172-173°C

IR: ν_{CHCl_3} (cm^{-1}): 3200, 1660, 1575, 1460, 1175, 1100, 1075, 1400 and 1350.

^{1}H-NMR (δ,$CDCl_3$): 0.88 (s,3H); 0.97 (s,3H); 2.33 (m,1H); 2.67 (m,1H); 7.38 (s,1H); 7.57 (d, J = 8 Hz, 2H); 7.85 (d, J = 8 Hz, 2H).

Preparation of Oxime of 28[39]

A mixture of the tricyclic pentanone 28 (68%, 0.74 mmole) and the cis diol 27 was dissolved in a ethanolic (3.0 ml)-pyridine (0.5 ml) solution. After the addition of hydroxylamine hydrochloride (200 mg, 2.8 mmoles), the reactants were refluxed for 1 hour. Then, the solvent was removed in vacuo to give an oil. Pentane was added to this product and the solid (126 mg) which formed was chromatographed on activity III, neutral alumina (10g). The diol 27 (53 mg) was eluted first (100% benzene) and identified by its ^{1}H-NMR, while the oxime (51 mg) was eluted next (25% ether-benzene). Attempts to crystallize the oxime for x-ray analysis resulted in granular crystals which were not suitable. The spectral data are as follows:

mp 73-80°C

IR: ν_{CHCl_3} (cm^{-1}): 3580, 3250, 1670, 1375.

^{1}H-NMR (δ,$CDCl_3$): 0.88 (s,3H); 0.99 (s,3H); 2.70 (m,2H).

Preparation of 5-Iodo-2-Nitrophenylhydrazone of Ketone 28[35]

A solution containing 5-iodo-2-nitrophenylhydrazide (82 mg, 0.3 mmole) in 95% ethanol (6.0 ml) containing one drop of sulfuric acid was added to the tricyclo ketone 28 (63 mg, 0.3 mmole) which was dissolved in 95% ethanol

(4.0 ml). The solution was concentrated on the steam-bath and the orange solid that formed upon cooling was filtered. Tlc of this product (benzene) showed one spot (R_t = 0.9). However, repeated crystallization of the solid to obtain a crystal for x-ray analysis resulted in chunky orange crystals which appeared twinned on the diffractometer. The physical and spectral properties appear below.

mp 120-123°C

IR: ν_{CHCl_3} (cm^{-1}): 3300, 1601, 1575, 1480, 1320 and 1050.

^{1}H-NMR (δ,$CDCl_3$): 0.95 (s,3H); 1.08 (s,3H); 2.57 (m,1H); 2.83 (m,1H); 7.07 (d,d, J_1 = 10 Hz, J_2 = 2 Hz, 1H); 7.83 (d, J = 10 Hz, 1H); 8.27 (d, J = 2 Hz, 1H); 11.12 (s,1H).

Mass spectrum: M^+ = 439 (13%); 57 (100%).

Reduction of Tricyclopentanone 28 with Lithium Aluminum Hydride

Solid lithium aluminum hydride (250 mg, 6.6 mmoles) was added to a solution of tricyclopentanone 28 in anhydrous ether (100 ml). After stirring at room temperature for 3 hours, the reaction was quenched by the slow addition of ice chips. More ether (25 ml) was added and the aqueous layer was separated. The ether was washed with water (3x20 ml), dried over magnesium sulfate, filtered and evaporated in vacuo to yield a low melting solid which appeared pure by glc analysis (Col I, 140°C, R_t = 2 min 12 sec). An analytical sample for elemental analysis and ORD was prepared by hot box

distillation. The physical and spectral properties of the tricyclic alcohol 29 are as follows:

bp 65-85°C/0.3 mm (hot box)

IR: ν_{CHCl_3} (cm^{-1}): 3600, 3450, 1475, 1390, 1120, 1090, and 1040.

^{1}H-NMR (δ,$CDCl_3$): 0.88 (s,3H); 0.93 (s,3H); 4.23 (d,d, J_1 = 8 Hz, J_2 = 5 Hz, 1H).

Mass spectrum: M^+-H_2O = 162 (98%), m/e 107 (100%).

ORD (c = 1.63, $CHCl_3$): $[\phi]_{700}$ = 55.2°, $[\phi]_{589}$ = 66.3° ($[\alpha]_{589}$ = 36.8°), $[\phi]_{500}$ = 99.4°, $[\phi]_{400}$ = 176.7°, $[\phi]_{300}$ = 386.5°.

Analysis ($C_{12}H_{20}O$): Calculated: C, 80.00; H, 11.11.
Found: C, 79.92; H, 11.18.

Attempted Preparation of the p-Iodobenzoate Derivative of Tricyclopentanol 29

Solid p-iodobenzoyl chloride [122 mg, 0.46 mmole, mp 60-62°C (lit. mp 65-70°C)[40]] was added to the tricyclopentanol 29 (130 mg, 0.73 mmole) which was dissolved in dry pyridine (0.9 ml). After stirring at 47°C for 48 hours, the reactants were poured over ice. When the ice had melted, ether (25 ml) was added. Then, the layers were separated and the ether was washed successively with 10% sulfuric acid solution (3x20 ml), water, saturated potassium bicarbonate solution (3x20 ml) and neutral to litmus with water. Finally, the ether was dried over magnesium sulfate, filtered and evaporated in vacuo to

yield a low melting solid with an ^{1}H-NMR identical to the starting alcohol 29.

Reduction of the Tricyclic Lactone 30 with Lithium Aluminum Hydride[41]

Solid lithium aluminum hydride (759 mg, 20.0 mmoles) was added to the tricyclic lactone 30 (411 mg, 2.0 mmoles) which was dissolved in anhydrous ether (25 ml). After stirring at room temperature for 17 hours, the reaction was quenched by the addition of ice chips and dilution with water (10 ml) and ether (25 ml). When the hydride was completely destroyed, the ether was separated, washed with water, dried over magnesium sulfate, filtered and evaporated in vacuo to give a white solid (369 mg). This was recrystallized from ethyl acetate-pentane (1:10) to give a product with one peak on glc (Col. I, 160°, R_t = 2 min 48 sec). An analytical sample was prepared by dissolving the solid in ethyl acetate and this solution was placed in an ethyl ether atmosphere leading to the solid crystallizing from the ether solution. The physical and spectral properties of the diol 31 appear below.

An attempt was made to do an x-ray structure on the colorless needles obtained. However, the diffractometer had difficulty in centering on a peak. It was found that the crystal was twinned.

mp 110-111°C

IR: ν_{CHCl_3} (cm^{-1}): 3610, 3420, 1470, 1380, 1230, 1075, 1050, 1020.

^{1}H-NMR (δ,$CDCl_3$): 0.92 (s,3H); 1.02 (s,3H); 2.32 (s,O-H); 3.18 (d,d, J_1 = 10 Hz, J_2 = 5 Hz, 1H); 3.45 (d, J = 5 Hz, 2H).

Mass spectrum: 180 (M^+-H_2O, 9%), 123 (98%), 139 (100%).

ORD (c = 1.37, $CDCl_3$): $[\phi]_{700}$ = -17.3°, $[\phi]_{589}$ = -34.7° ($[\alpha]_{589}$ = -17.5°), $[\phi]_{500}$ = -49.1°, $[\phi]_{400}$ = -72.3°, $[\phi]_{300}$ = -112.7°.

Analysis ($C_{12}H_{22}O_2$): Calculated: C, 72.68; H, 11.18.
Found: C, 72.68; H, 11.21
C, 72.64; H, 11.18.

Preparation of p-Iodobenzoate of Diol 31

The diol 31 (132 mg, 0.67 mmole) was dissolved in dry pyridine (1.0 ml). Then p-iodobenzoyl chloride (184 mg, 0.69 mmole, mp 60-62°C (lit mp 65-70°C)[26]] was added. After stirring at room temperature for 17 hours, the reactants were poured over ice and ether (25 ml) was added when the ice had melted. The ether was separated and successively washed with 10% sulfuric acid (3x20 ml), water, saturated potassium bicarbonate solution (3x20 ml), water until neutral to litmus, dried over magnesium sulfate, filtered and evaporated in vacuo to yield a viscous oil which was further purified by chromatography on activity III alumina eluting with ether-benzene (1:4) to give a solid product (177 mg). A

white flocular solid (mp 118-119°C) was obtained from crystallization in benzene.

The following are the spectral properties:

IR: ν_{CHCl_3} (cm^{-1}): 3610, 3450, 1725, 1475, 1400, 1600, 1180, 1120, 1130, 1020, 900.

^{1}H-NMR (δ,$CDCl_3$): 0.93 (s,3H); 1.03 (s,3H); 3.20 (m,1H); 4.27 (d, J = 6 Hz, 2H); 7.83 (s,4H).

Oxidation of Lactone 30 with Ruthenium Tetroxide[42]

The lactone 30 (96.1 mg, 0.49 mmole) was dissolved in 0.17 N sodium hydroxide (2.9 ml, 0.49 mmode) by heating on a steam-bath for two hours. Then ruthenium chloride (6 mg) was added at room temperature turning the solution black. Aqueous sodium metaperiodate (104 mg/3.0 ml, 0.49 mmole) was added in small increments. After each addition, the solution turned colorless and slowly back to black. After all of the sodium metaperiodate had been added and the yellow color persisted for 30 minutes, a few drops of isopropanol were added turning the solution black as the alcohol was oxidized.

The solution was made basic to litmus with cold IN sodium hydroxide and extracted with ethyl acetate (3x20 ml). The combined ethyl acetate fractions were washed until neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated in vacuo to give a white solid (39.9 mg) that was mainly lactone 30 as shown by ^{1}H-NMR.

The basic portion was acidified and extracted with

ethyl acetate after saturation with salt. The combined ethyl acetate extracts were washed until neutral to litmus with dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a brown oil (25.1 mg). Its IR showed broad carboxylic acid absorption from 2500 to 3600 cm^{-1} and a broad carbonyl at 1700 to 1750 cm^{-1}, while the proton NMR had only two discernible signals for methyls at δ 0.90 and 1.00. These spectra show that oxidation did occur but in low yield.

Preparation of Daucol (3) from Carotol (1)

Carotol (1) (1.00g, 4.54 mmoles) was dissolved in methylene chloride (40 ml) and chilled to 0°C. Then, m-chloroperbenzoic acid (1.55g, 9.0 mmoles) in methylene chloride (40 ml) was added to the magnetically stirred solution of the above over a 15 minute period. Stirring was continued for one hour at 0°C. Then, saturated sodium bisulfite solution (40 ml) was added and stirring continued for 15 minutes until the solution was negative to starch iodide paper. The methylene chloride layer was separated and washed with saturated sodium bicarbonate solution (2x40 ml) followed by water and then saturated salt solution (40 ml), dried over magnesium, filtered and evaporated *in vacuo* to give a white solid with one major peak (R_t = 5 min 28 sec) and two minor peaks (R_t = 7 min 24 sec, 8 min 24 sec) by analysis with glc (Col I, 160°C).

Crystallization from benzene-hexane gave a white solid (427 mg) with one peak on glc and mp 110-117°C (lit mp 118°C).[2,3,10] Sublimation (35°C/0.05 mm) gave a white solid (239 mg) (mp 119-121°C) with the following spectral properties:

*IR ν_{nujol} (cm^{-1}): 3500-3050, 1050.

*^{1}H-NMR (δ,$CDCl_3$): 0.85 (d, J = 6 Hz, 6H); 1.10 (s,3H); 1.37 (s,3H); 3.83 (m,1H).

^{13}C-NMR (δ,$CDCl_3$): 45.50 (quaternary), 5230, 71.17 (-C-OH), 84.94 (-C-OR), 91.13 (-C-OR), 21.66, 22.33, 22.81, 23.36, 26.21, 29.36, 31.37, 32.88, 40.83, 41.01.

Mass spectrum: M^+ = 238 (4%), m/e = 151 (100%).

Air Oxidation of Carotol (1) to Yield Daucol (3)

After standing for several months, a bottle that contained remnants of carotol (1) had a fluffy white solid coating a gummy substance on its bottom. The melting point (110-112°C) along with comparison of its glc (Col I, 165°C), ^{1}H-NMR, IR and mass spectrum proved that this solid was daucol (3). The spectral properties appear above.

Tosylation of Daucol (20)[41]

Solid p-toluenesulfonyl chloride (125 mg, 0.66 mmole) was added to a magnetically stirred solution of daucol (20)

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*IR and ^{1}H-NMR agree with published values.[2,3,10]

(105 mg, 0.44 mmole)) in pyridine (1.0 ml). [The tosyl chloride (5.0g) had been crystallized by dissolving it in chloroform (10 ml) and adding petroleum ether (50 ml). After decolorizing with charcoal and filtering, it was concentrated on the steam-bath to give white crystals, mp 68-70°C (lit. mp 69-71°C[16]]. The reactants were kept in the dark for 11 days, then they were poured over ice. After the ice had dissolved, the solution was extracted with ether (3x20 ml) and the combined ether extracts were washed with water (5x20 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo* with intermittent addition of hexane until no more pyridine remained to give a viscous oil (159 mg , 0.41 mmole) which gave one spot (R_t = 0.5) by tlc (hexane-benzene 1:1). The spectral properties of the tosylate 34 are as follows:

IR: ν_{neat} (cm^{-1}): 1590, 1170, 1380, 1100.

H^1-NMR, (δ,$CDCl_3$): 0.81 (d, J = 6 Hz, 3H); 1.02 (d, J = 6 Hz, 3H); 1.03 (s,3H); 1.15 (s,3H); 2.44 (s,3H); 4.55 (q,1H); 7.58 (d , d, 4H).

Mass spectrum: M^+ = 392 (2%), m/e = 193 (100%).

Analysis ($C_{22}H_{32}O_4S$): Calculated: C, 67.31; H, 8.22.
Found: C, 67.30; H, 8.23.

Reaction of Daucol Tosylate (34) with Lithium Aluminum Hydride

Daucol tosylate (34) (126 mg, 0.32 mmole) was dissolved

in anhydrous tetrahydrofuran (10 ml), and lithium aluminum hydride (144 mg, 3.9 mmoles) was added with stirring at room temperature. When the bubbling had subsided, the reactants were heated at 58°C for 4 days. Then, saturated sodium potassium tartrate followed by ether (10 ml) was added. The organic layer was separated, washed with water (3x15 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo*. The glc (Col I, 160°C), IR and ^{1}H-NMR were identical to those of daucol (*3*).

Reduction of Daucol Tosylate (*34*) with Lithium Triethylborohydride[43]

Daucol tosylate (*34*) (164 mg, 0.42 mmole) in freshly distilled tetrahydrofuran (4.0 ml), followed by lithium triethylborohydride (2.0 ml, 1.0 M in tetrahydrofuran), was added to a dry three-necked flask under nitrogen. Stirring was continued at room temperature for 17 hours. Then water (1.0 ml), 1 N sodium hydroxide solution (2.0 ml) and 30% hydrogen peroxide (2.0 ml) were added.

After stirring for 30 minutes, saturated salt solution (20 ml) was added and this was extracted with ether (3x20 ml). The combined extracts were washed until neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated *in vacuo* to give an oil with an IR and ^{1}H-NMR identical to the starting tosylate *34*.

X-ray Structures

Tricyclocarotol p-Iodobenzoate (22)

Crystal data $C_{22}H_{29}O_2I$; MW452.4

$a = 13.21(1)^*$, $b = 12.40(1)$, $c = 13.82(1)$

$\alpha = 90.00°$, $\beta = 112.84(1)°$, $\gamma = 90.00°$

$V_c = 2085(1)\text{Å}^3$; $z = 4$; $D_c = 1.44\ gcm^{-3}$

Space group: $P2_1/C^{44}$ (monoclinic, #14 from systematic absences) h00: no conditions; h01: 1 = 2n; 0k0: k = 2n

$2\theta_{max} = 50.0°$ ($MoK\alpha_1$, $\lambda = 0.71069\text{Å}$)

Independent reflections: 2665; 2637 $\geq$ 36(I)

Room temperature: 25°C

$R = 0.058$, $R_w = 0.046$

The crystals were obtained from ethyl acetate in the form of large plates and a piece (0.42 x 0.48 x 0.98 mm) was used for the x-ray analysis. Intensity data were collected on a Syntex P_{21} four-circle computer controlled diffractometer with graphite monochromated M_o-K_α radiation. Unit-cell dimensions were determined from the least squares refinement of three instrumental angles for 15 centered reflections; and the structure was solved using Patterson methods and refined using anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters (5.0) for hydrogen atoms. The refinement converged

*Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

to R = 0.058 and R_w = 0.046 with the final atomic parameters in Table 9 and Table 10; while anisotropic temperature factors are in Table 11 and the structure factors are included in Table 19 of the Appendix, while selected distances and angles are in Table 15 and Table 16 of the discussion, which also includes an ORTEP drawing, Figure 3, of the molecule.

Tricyclodaucene Diol (23)

Crystal data

$C_{15}H_{26}O_2$; MW238

a = 9.86(1), b = 13.76(1), c = 10.26(1)Å

$\alpha = \beta = \gamma = 90°$

V_c = 1389Å^3; z = 4; D_c = 1.09 gcm^{-3}

Space group: $P2_12_12_1$ [44] (orthorhombic, #19, from systematic absences, h00, h = 2n+1; 0k0, k = 2n+1; 001, l = 2n+1

$2\theta_{max}$ = 50° (MoK_α, λ = 0.71069Å)

Independent reflections: 1461; 792 $\geq$ 36(I)

Room temperature: 25°

R = 0.106, R_w = 0.084

Intensity data were collected as with the ester 22. Unit cell dimensions were determined from the least squares refinement of three instrumental angles for 15 centered reflections. The structure was solved using direct methods and refined to convergence at R = 0.106 and R_w = 0.084. All of the carbons and oxygens were located from an E map using phases generated by the Multan Program, while hydrogens

were located from the subsequent difference Fourier. Variables included a scale factor, coordinates for all carbon and oxygen atoms, anisotropic thermal parameters for oxygen and selected carbon atoms and isotropic thermal parameters for the remaining carbon atoms. A fixed thermal parameter (5.0) was used for the hydrogen atoms.

Final atomic parameters are given in Tables 12, 13 and 14 and the structure factors are included in Table 20 of the Appendix, while selected distances and angles are in Tables 17 and 18 of the discussion along with Figure 6 an ORTEP drawing (mirror image).

Table 9. Tricyclocarotol p-Iodobenzoate (22) Atomic Coordinates ($X10^4$) for Anisotropic Refinement

Atom	x	y	z
I	-4647(3)	3655.9(6)	6300.4(4)
01	-5152(2)	3257(3)	1677(2)
02	-3905(2)	3249(4)	924(3)
BC1	-3299(4)	3419(4)	2781(4)
BC2	-3567(4)	3365(4)	3649(4)
BC3	-1679(4)	3353(5)	4781(4)
BC4	-1413(4)	3617(6)	3929(5)
BC5	-2764(4)	3432(5)	4649(4)
BC6	-2208(4)	3551(6)	2925(5)
CCAR	-4130(4)	3300(4)	1685(4)
HBC2	- 423(4)	329(4)	354(4)
HBC3	- 73(4)	365(4)	405(4)
HBC5	- 291(4)	334(4)	519(4)
HBC6	- 212(4)	351(4)	234(4)
C1	-7127(3)	3486(4)	944(3)
C2	-7294(4)	2613(5)	1664(4)
C3	-6696(5)	1597(5)	1537(5)
C4	-8292(5)	2285(6)	- 550(5)
C5	-7291(6)	1625(6)	- 416(5)
C6	-8011(4)	3454(5)	- 218(4)
C7	-7383(5)	3902(5)	- 864(4)
C8	-6172(4)	3632(5)	- 274(4)
C9	-6133(3)	3065(4)	722(3)
C10	-6337(4)	1835(4)	629(4)
C11	-5343(6)	1155(6)	689(6)
C12	-9069(5)	4084(8)	- 421(5)
C13	-6891(5)	4561(5)	1576(5)
C14	-7811(7)	4903(7)	1940(6)
C15	-6564(9)	5539(7)	1115(7)

Table 10. Tricyclocarotol p-Iodobenzoate (22) Atomic Coordinate ($x10^3$) for Hydrogen Atoms*

Atom	x	y	z
HC2A2	-695(4)	283(4)	240(4)
HC2B2	-806(4)	249(4)	150(4)
HC3A	-607(4)	138(4)	220(4)
HC3B	-722(4)	115(4)	136(4)
HC4A	-702(4)	179(4)	- 99(4)
HC4B	-744(4)	100(4)	- 47(4)
HC5A	-879(4)	229(4)	-125(4)
HC5B	-866(4)	193(4)	- 10(4)
HC7A	-744(4)	454(4)	- 93(4)
HC7B	-722(4)	353(4)	-162(4)
HC8A	-564(4)	409(4)	- 7(4)
HC8B	-596(4)	317(4)	- 70(4)
HC11A	-462(4)	122(4)	140(4)
HC11B	-519(4)	130(4)	5(4)
HC11C	-552(4)	43(5)	59(4)
HC12A	-898(4)	495(4)	- 10(4)
HC12B	-955(4)	389(4)	-106(4)
HC12C	-946(4)	393(4)	6(4)
HC13	- 28(4)	388(4)	-254(4)
HC14A	-747(4)	522(4)	253(4)
HC14B	-820(4)	430(4)	205(4)
Hc14C	-837(4)	534(4)	139(4)
HC15A	-577(4)	532(4)	107(4)
HC15B	-639(4)	604(4)	174(4)
HC15C	-722(4)	563(4)	60(4)

*B = 5.0.

Table 11. Tricyclocarotol p-Iodobenzoate (22) Anisotropic Temperature Factors ($x10^4$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	81(3)	2629(9)	990(3)	341(4)	8(2)	-47(5)
O1	63(2)	66(3)	640(2)	00(2)	33(2)	1(2)
O2	86(3)	159(5)	810(3)	2(3)	53(2)	- 1(3)
BC1	67(3)	52(4)	780(4)	6(3)	39(3)	10(3)
BC2	59(3)	67(5)	84(4)	- 1(3)	36(3)	- 2(3)
BC3	71(4)	106(6)	87(4)	15(4)	29(3)	13(4)
BC4	55(3)	148(7)	117(5)	13(4)	32(3)	26(5)
BC5	72(3)	91(6)	74(4)	5(4)	33(3)	6(4)
BC6	72(4)	123(6)	94(4)	19(4)	42(3)	21(5)
CCAR	74(4)	73(5)	75(4)	- 1(3)	41(3)	2(3)
C1	67(3)	77(5)	48(3)	1(3)	31(2)	- 6(3)
C2	70(3)	95(5)	59(3)	- 8(4)	37(3)	3(4)
C3	107(4)	77(5)	81(4)	- 25(4)	51(3)	1(4)
C4	142(6)	79(6)	81(4)	- 35(5)	55(4)	-21(4)
C5	99(5)	130(7)	65(4)	- 33(5)	16(3)	-18(4)
C6	79(4)	121(6)	52(3)	8(4)	20(3)	2(4)
C7	120(5)	90(6)	59(3)	11(4)	30(3)	15(4)
C8	93(4)	83(5)	60(3)	- 7(4)	42(3)	-00(4)
C9	70(3)	52(4)	52(3)	- 1(3)	30(2)	- 5(3)
C10	104(4)	51(5)	72(4)	- 3(4)	46(3)	- 3(3)
C11	150(6)	41(5)	123(5)	11(4)	75(5)	- 7(4)
C12	13(5)	215(10)	73(4)	48(6)	12(3)	- 5(5)
C13	126(5)	66(5)	93(4)	12(4)	65(4)	- 9(4)
C14	138(6)	133(7)	101(5)	62(6)	53(5)	-11(5)
C15	231(10)	98(7)	134(7)	18(7)	83(7)	-32(6)

Table 12. Diol 23 Final Positional and Thermal Parameters ($X10^4$) of Carbon Atoms Varied Isotropically

Atom	x	y	z	B($\AA^2$)
C2	3965(13)	8433(9)	3648(13)	5.2(3)
C3	3270(11)	7807(7)	2506(10)	3.8(2)
C4	4547(11)	7518(7)	1616(10)	3.2(2)
C5	4206(13)	6707(8)	621(11)	4.7(3)
C6	2847(12)	6256(6)	704(9)	3.3(2)
C7	2320(11)	6089(7)	2104(11)	3.5(2)
C8	3015(10)	6769(6)	3091(9)	2.9(2)
C9	4484(12)	6414(8)	3467(11)	4.2(3)
C10	5410(13)	7171(9)	2782(13)	5.5(3)
C11	2144(12)	8346(8)	1818(11)	4.2(3)
C12	2650(13)	9228(9)	970(12)	5.6(3)
C15	820(12)	6116(7)	2130(11)	4.4(3)

Table 13. Diol 23 Final Positional and Thermal Parameters of Carbon and Oxygen Atoms Varied Anisotropically

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
01	2698(8)	5090(4)	2377(6)	171(12)	25(3)	103(9)	-91(5)	00(9)	3(4)
02	2812(10)	5383(4)	-49(6)	283(17)	38(4)	81(8)	- 2(7)	-10(10)	-18(4)
C1	5404(18)	8094(8)	3654(13)	279(31)	69(9)	124(16)	-22(14)	-104(20)	4(11)
C13	1064(15)	8687(8)	2837(14)	225(24)	54(8)	181(18)	19(11)	-37(19)	-26(11)
C14	6844(15)	6802(11)	2492(18)	163(24)	116(12)	250(27)	- 4(13)	-50(22)	23(14)

Table 14. Diol 23 Final Positional Parameters ($X10^2$) of the Hydrogen Atoms*

Atom	x	y	z
HC1	60	78	42
HC2A	34	82	44
HC2B	34	92	34
HC4A	48	82	10
HC4B	40	78	22
HC5A	46	70	- 4
HC5B	52	64	6
HC6	22	68	4
HC8	26	70	40
HC9A	46	58	28
HC9B	48	66	44
HC11	12	82	16
HC12	16	94	10
HC13A	00	90	26
HC13B	20	92	34
HC14A	68	64	18
HC14B	74	70	38
HC14C	70	78	24
HC15A	4	68	20
HC15B	2	62	28
HC15C	2	56	16
HO1	36	50	24
HO2	38	54	2

*Temperature factor is constant, B = 5.0.

Preparation of 49[54]

A solution of cis and trans nerolidol (47) (44.4g, 0.20 mmole, Hoffman-La-Roche, Lot 001024) and N-bromo-succinimide (37.4g, 0.22 mmole) recrystallized (according to the method of Dauben[55]) in dry carbon tetrachloride (40 ml) was stirred at room temperature for five days, then petroleum ether (bp 30-60°C, 500 ml) was added to the reactants and the white precipitate which formed was removed by filtration through Cellite. After adding freshly distilled collidine (97g), the solution was reduced to a constant volume in vacuo. The remaining liquid was heated under nitrogen one hour at 110°C and then at 160°C for three hours.

After cooling to room temperature 10% hydrochloric acid solution was added to the reactants until the solution was acid to litmus. The product was extracted with ether (3x150 ml); and the combined ether fractions were washed until neutral to litmus with water, dried over magnesium sulfate and evaporated in vacuo to yield a brown oil (45.8g). Glc analysis (Col IV, 170°C) showed one major peak (R_t = 1 min 36 sec) and several minor ones. Short path distillation gave a major fraction (17.1g, 85-95°C/0.5 mm) containing 85% of the desired cycloheptenone (49). Infrared and ^{1}H-NMR spectra were similar to those reported by Demole[54], while the ^{13}C-NMR and mass spectra were like those of Clower.[24]

IR: ν_{neat} (cm^{-1}): 1700, 1580, 750.

^{1}H-NMR (δ,$CDCl_3$): 1.05 (s,3H); 1.55 (s,3H); 1.63 (s,6H);

5.05 (s,1H); 5.45 (m,1H).

^{13}C-NMR (δ,$CDCl_3$): 215.9, 136.6, 131.5, 124.3, 121.6, 53.7, 39.0, 37.9, 35.1, 32.0, 25.6, 25.2, 23.0, 22.1, 17.5.

Mass spectrum: M^+ = 220 (1%); m/e = 138 (100%).

Preparation 50

The cycloheptenone (49) (5.0g, 0.022 mmole) was dissolved in anhydrous ether (200 ml) and cooled to 0°C in an ice-bath. Then lithium aluminum hydride (9.0g, 0.24 mole) was slowly added. After the solution was warmed to room temperature, stirring was continued for 3.5 hours. It was then cooled to 0°C and 10% ammonium chloride solution was added until the frothing stopped. Stirring was continued for 1.5 hours. The ether layer was removed and the aqueous was extracted with ether (3x100 ml). Then, the combined ether fractions were washed with water (4x100 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield an oil (4.3g) which was 85% pure by glc (Col IV, 170°C). Chromatography on silica gel (250g) gave an alcohol fraction (3.2g, 50% benzene-hexane eluent) which was shown by ^{1}H-NMR to be a mixture of isomers 50. The spectra which appear below agree with those of Clower.[24]

IR: ν_{neat} (cm^{-1}): 3400, 1015.

^{1}H-NMR (δ,$CDCl_3$): 0.82, 0.98 (s, 1:2 ratio, 3H); 1.57 (s,3H); 1.63 (s,3H); 1.70 (s,3H); 3.48 (m,1H); 5.25 (m,2H).

^{13}C-NMR (δ,$CDCl_3$): 140.1, 130.9, 125.4 and 122.4, (C=C),

81.2, 39.7, 39.1, 34.8, 33.4, 29.7, 28.5, 25.7, 25.3, 24.3, 22.3, 17.5.

Mass spectrum: M^+ = 222 (16%), m/e = 41 (100%).

Attempted Tosylation of Cycloheptenol 50[56]

The cycloheptenol 50 (1.00g, 4.5 mmoles) was dissolved in dry pyridine (5.0 ml). After heating to 60°C, tosyl chloride (1.71g, 9.0 mmoles) was added. This solution was heated for 24 hours, at which time the solution was poured over ice. When the ice had melted, the product was extracted with chloroform (3x31 ml). Then, the combined chloroform extracts were washed with saturated salt solution (4x50 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo* leaving a brown oil (0.74g). Absence of absorption at 3500-3300 cm^{-1} in the infrared spectrum showed that the hydroxyl had reacted. However, there was no absorption in the aromatic region, indicating that tosylate had not formed. An absorption at 1640 cm^{-1} showed the presence of unconjugated olefins. The ^{1}H-NMR spectrum did not have any signals in the aromatic region. Signals that were present were (δ,$CDCl_3$) 1.60-1.65 (m,12H) for olefinic methyls and 4.70 (s,1H), 5.07-5.33 (m,2H) for olefinic protons.

Mesylation of Cycloheptenol 50[56]

Cycloheptenol 50 (128 mg, 0.58 mmole) was dissolved in dry pyridine (0.6 ml); then mesylchloride (0.1 ml, 150 mg, 1.2 mmole) was added and the reactants were heated at 60°C

for 2 hours. To quench the reaction the mixture was poured over ice. When the ice had melted, the aqueous solution was extracted with chloroform (3x25 ml). Then the combined chloroform extracts were washed with portions of a 5% hydrochloric acid solution (50 ml), 5% sodium bicarbonate solution (3x25 ml), neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a brown oil (168 mg), the mesylate **49** which was used as such for subsequent experiments. It had the following spectral properties:

IR: ν_{neat} (cm^{-1}): 1670, 1640, 1380 and 1170.

^{1}H-NMR (δ,$CDCl_3$): 0.93, 1.18 (s, 1:2 ratio, 3H); 1.57-1.83 (m,9H); 1.73 (s,3H); 2.93 (s,3H); 4.70 (m,1H); 5.23 (m,1H).

Formolysis of Cycloheptenone 49 Followed by Reduction of the Product

The cycloheptenone **49** (142 mg, 0.64 mmole) was stirred with 90% formic acid (2.0 ml) which was 0.5 M in sodium formate for 14 days. After pouring the reactants over ice, 10% sodium hydroxide solution was added. The basic solution was extracted with ether (3x20 ml) and the combined ether extracts were washed neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated *in vacuo* to give a brown oil (134 mg). Analysis by glc (Col IV, 170°C) showed one major peak (R_t = 3 min 16 sec) and six minor

peaks including one for unreacted cycloheptenone 49. The infrared spectrum had distinctive absorbancies at 3400, 1720, 1700 and 750; while the ^{1}H-NMR had discernible signals corresponding to unreacted ketone 49 plus a singlet at δ 1.18.

The above product (134 mg) was dissolved in anhydrous ether (3.0 ml). Then lithium aluminum hydride (235 mg, 6.2 mmole) was added while stirring at 0°C. After ten minutes the ice-bath was removed and stirring continued at room temperature for two hours. The reaction was quenched by the addition of water which was extracted with ether (3x15 ml). The combined ether extracts were washed with water, dried over magnesium sulfate, filtered and evaporated in vacuo to yield an oil (83 mg). Glc analysis (Col IV, 170°C) showed one major peak (R_t = 3 min 12 sec), two minor peaks (R_t = 1 min 9 sec, 1 min 57 sec) and several very small ones. Absence of carbonyl absorption in the infrared spectrum indicated that the reduction was complete. The product was chromatographed on silica gel (4.0g) to give a substance (36 mg) containing the major peak and a minor one by glc (Col IV, 170°C) in the benzene-hexane (1:1) eluent and it had the following spectral properties:

IR: ν_{neat} (cm^{-1}): 3400, 1450, 1375 and 750.

^{1}H-NMR (δ,$CDCl_3$): 0.88, 1.03 (s, ratio 1:2, 3H); 1.20-1.47 (m,9H); 3.50 (m,1H); 5.23 (m,1H).

Formolysis of Cycloheptenol 50

Cycloheptenol 50 (98 mg, 0.44 mmole) was stirred in 90% formic acid (2.0 ml) for 20 minutes at room temperature. Then, the reactants were poured into ice-water (20 ml). Addition of 10% sodium hydroxide solution (19 ml) was followed by extraction with ether (3x25 ml). The combined ether extracts were washed until neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a colorless oil (96 mg). Glc analysis of this product (Col IV, 170°C) showed that unreacted cycloheptenol 48 (R_t = 2 min 185 sec) and a major product (R_t = 2 min 48 sec) as well as seven minor products were present.

Chromatography on silica gel (10g) gave pure alcohol 48 (19 mg, benzene eluent) whose infrared and ^{1}H-NMR spectra agree with those already reported.[24] A second fraction (21 mg, benzene-hexane 1:1 eluent) contained the second major substituent. Absence of absorption at 3400 cm^{-1} and strong absorption at 1725 cm^{-1} in its infrared spectrum indicated formation of the formate ester which had the following spectrum:

^{1}H-NMR (δ,$CDCl_3$): 0.90, 0.92 (s ratio 1:2, 3H); 1.60 (s,3H); 1.77 (s,3H); 1.73 (s,3H); 4.82-5.67 (br. m, 2H).

Formolysis of the cycloheptenol 50 for 45 minutes at room temperature or at 60°C for 3 minutes resulted in mixtures too complex to analyze beyond glc (Col IV, 170°C.

Saponification of the Formate Ester of 50

The formate ester was dissolved in 2N methanolic sodium hydroxide solution. After refluxing for four hours, the reactants were poured into water and acidified with 10% hydrochloric acid solution and the product was extracted with ether (35 ml) for 22 hours using a continuous liquid-liquid extractor. The ether layer was separated, dried over magnesium sulfate, filtered and evaporated by distillation of the ether through a vigreux column to yield the product (16 mg). The glc (Col IV, 170°) and infrared and ^{1}H-NMR spectra all agreed with those previously reported for cycloheptenol 50.

Acetolysis of Mesylate 51

The mesylate 51 (202 mg, 0.68 mmole) was stirred with 0.5 M potassium acetate in acetic acid (2.0 ml) at room temperature for 22 hours. Then, the reactants were diluted with water, the acid was neutralized with 10% sodium hydroxide solution and this solution was extracted with ether (3x25 ml). The combined ether extracts were washed with water (3x25 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a yellow oil (121 mg).

Analysis by glc (Col IV, 170°C) gave two major peaks (R_t = 1 min 12 sec, 1 min 24 sec), which were about 90% of the volatile product. Distinctive absorptions in the infrared spectrum were at 1730, 1440, 1375 and 750 cm^{-1}. The ^{1}H-NMR

had the following characteristic signals:

(δ,$CDCl_3$): 1.25-1.47 (m,3H); 1.60-1.83 (m,9H); 4.77-5.50 (m,2H).

The mass spectrum of the mixture had m/e 93 (100%) and M^+ = 204 (30%).

Acetolysis at 118°C for three hours and at 60°C for 20 minutes resulted in the same final mixture; while the product resulting from acetolysis at room temperature for as long as three hours still contained starting mesylate as well as the above mixture.

Formolysis of Mesylate 51

The mesylate 51 (550 mg, 1.83 mmole) was stirred with 90% formic acid (4.0 ml) for 20 minutes, then the reactants were poured over ice. Addition of 10% sodium hydroxide solution (35 ml) was followed by extraction with ether (3x50 ml). The combined ether extracts were washed with water (3x20 ml), dried over magnesium sulfate, filtered and evaporated *in vacuo* to yield a brown oil (410 mg). Glc analysis of the crude product (Col IV, 170°C) showed two major peaks (R_t = 1 min 18 sec, 1 min 30 sec) and several minor ones; while the infrared spectrum had characteristic absorbancies at 3400, 1725, 1440 and 1375 cm^{-1}. The ^{1}H-NMR had the following signals (δ,$CDCl_3$); 1.20 (s,3H); 1.33-1.77 (m,6H); 4.78-5.30 (m,3H).

Glc analysis (Col IV, 170°C) of the product from

formolysis of the mesylate 49 at room temperature for three days showed the same product composition as for 20 minutes.

Hydrolysis of Formate Ester from Formolysis of Mesylate 51

The crude product (110 mg) from the formolysis of the mesylate 51 was dissolved in 95% ethanol (50 ml) containing 15% sodium hydroxide solution (40 ml) and stirred at room temperature for 2.5 hours. After diluting with saturated salt solution, the product was extracted with ether (4x100 ml). The combined ether extracts were washed until neutral to litmus with water, dried over magnesium sulfate, filtered and evaporated in vacuo to give an oil (389 mg) which had two major peaks which were in the olefinic region by glc analysis (Col IV, 170°C, R_t = 1 min 36 sec, 1 min 48 sec) and several minor peaks. The tracing of the previous product looked basically identical. The only changes in the infrared spectrum from the product before hydrolysis was a stronger absorbancy at 3400 cm^{-1}, disappearance of the one at 1725 and a new one at 850 cm^{-1}. The ^{1}H-NMR spectrum retained the same characteristic signals.

Chromatography of a portion (100 mg) of the above product on silica gel (10g) gave one major fraction (33 mg, hexane eluent) which on glc analysis (Col IV 170°) had two peaks in the olefinic region. The infrared spectrum did not show distinctive features which would be characteristic of any functional groups. The ^{1}H-NMR had a complex multiplet

(δ,$CDCl_3$) 1.50-1.77 (12H) for olefinic methyls and a multiplet at 4.77-5.53 (3H) for olefinic protons. The mass spectrum of the olefinic mixture had a peak m/e 119 (100%) and M^+ = 204 (66%).

CHAPTER IV

DISCUSSION

During the formolysis of carotol (1) the initially formed daucene (9) and acoradienes (16) disappear with time and five other products which were detected by glc and separated by column chromatography on silica gel are formed according to the reaction sequence in Figure 2.[24,45] They consist of two tricyclic olefins, tricyclodaucene (17) and isotricyclodaucene (18), daucane ether (19), tricyclocarotol (20) and tricyclocarotol formate (21). The structure of tricyclocarotol (20) was determined by examination of spectral data and x-ray analysis of its p-iodobenzoate 22 derivative. That of tricyclodaucene (17) was elucidated by spectral evidence from the olefin and several reaction products, then confirmed by the x-ray analysis of its cis diol 23. The structure of the second olefin, isotricyclodaucene (18), was determined from spectral properties along with those of reaction and degradation products, while daucane ether (19) is assigned its structure from spectral evidence.[24]

After the separation and characterization of the tricyclic alcohol 20 and its formate ester 21, it was found that a mixture of the two could be treated with lithium aluminum hydride to produce one product, tricyclocarotol (20).[24]

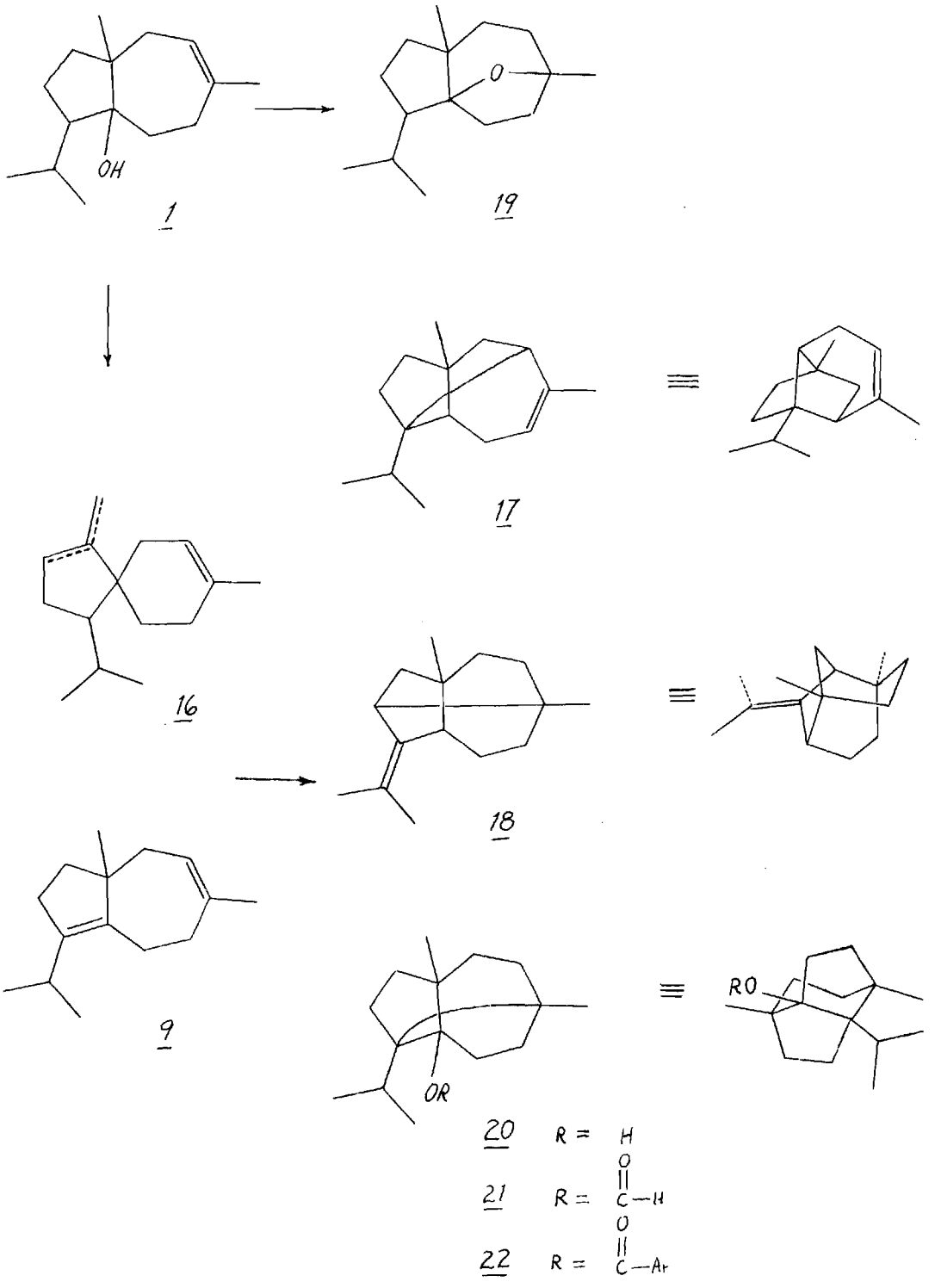

Figure 2. Products Formed in the Formolysis of Carotol (1)

Therefore, the ester 21 has the same skeleton as the alcohol 20 and determination of the structure of the latter would result in identification of both compounds. The IR, NMR (^{1}H and ^{13}C), mass spectrum, elemental analysis and ORD showed that the substance was an optically active tricyclic tertiary alcohol ($C_{15}H_{26}O$) containing four quartenary carbon atoms and four methyl groups.

Since the ^{1}H-NMR consisted of overlapping doublets and singlets it was difficult to make assignments. Clower,[24] using the shift reagents Eu $(dpm)_3$ and Eu $(fod)_3$, was able to elucidate the nature of the various methyl groups. The signal (s, δ 0.85) belonging to the protons on the methyl closest to the alcohol-europium complex moves downfield (δ 5.30)* the most rapidly and therefore is assigned to (C11)$\underline{H}_3$ while the signal for the protons (s, δ 0.93) shifted the least (δ 2.88) is attributed to (C12)$\underline{H}_3$ as it is the farthest away. Since the isopropyl group is not free to rotate rapidly, the methyls are unequivalent with the signal (δ 1.02) for the one (C14)$\underline{H}_3$ closest to the hydroxyl shifted the most (δ 3.78) while that for (C15)H_3 (d, δ 1.15) is shifted (δ, 3.03) to a lesser extent.

With the structure known it is also possible to assign values for ^{13}C-NMR shifts which are differentiated in the off resonance decoupled spectrum. Signals for the quaternary

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*Eu(fod)$_3$/alcohol (2.96 to 1.00).
**Numbering is on Figure 4.

carbons, in this case, are singlets and are the only ones separated enough to be given assignments. These were made by applying chemical shift rules.[46] First, the one farthest downfield at δ 91.7 is attributed to C9, the carbon bearing the hydroxyl, the next δ60.2 to C1, δ48.5 to C10 and δ47.4 to C6.

Further evidence for the structure came from the fact that in the mass spectrum the base peak m/e 179 corresponds to loss of an isopropyl group (M^+-C_3H_7) and an intense peak (78%) at m/e 161 indicates the loss of water also (M^+-C_3H_7-H_2O). A more thorough discussion of the mass spectrum is included later with respect to daucanes 2 in general.

The approach taken to prove the structure of the alcohol 20 was to synthesize a crystalline derivative for x-ray analysis. Since tricyclocarotol (20) is a hindered tertiary alcohol, it was difficult to make an ester derivative from it. The reaction of bromo acetyl bromide in dimethyl aniline resulted in a product with a complex ^{1}H-NMR indicating the occurrence of side reactions, while benzoyl chloride in dimethyl aniline and β-bromopropionyl isocyanate in chloroform resulted in unreacted alcohol 20 as indicated by broad absorbance at 3400 cm^{-1} in their infrared spectra. It was then decided to use more stringent reaction conditions. The lithium salt of 20 was prepared with butyl lithium in dimethoxyethane. Then, p-iodobenzoyl chloride was added. As small amounts of water seemed to affect the reaction when it was

carried out on a small scale, the derivative was eventually made using larger quantities (1.0g) of tricyclocarotol (20). The crude ester 22 was purified by silica gel chromatography until there was one spot on tlc and one peak on glc. However, the solid had a broad melting range (70-88°C). Its spectral properties, though, were consistent with the structure of the ester 22. The IR had absorbancies at 1725 (C) and 1580 (phenyl) cm^{-1} indicating that the ester had formed. While the ^{1}H-NMR had two singlets (δ0.87 and 1.02) for the quartenary methyls and two doublets (δ1.07 and 1.10) for the isopropyl methyls along with a multiplet (δ7.75) for the aromatic protons indicating that the ester had formed without skeletal rearrangement of the alcohol 20. This was proved by reduction of the ester 22 with lithium aluminum hydride which resulted in the recovery of tricyclocarotol (20) with the same spectral properties as already described. Further confirmation came from the mass spectrum which had a molecular ion at m/e 452 (<0.01%) and base peak m/e 161 corresponding to loss of the isopropyl and p-iodobenzoate moieties. A crystal (mp 101-103°) suitable for x-ray analysis was finally obtained by crystallization from ethyl acetate.

The structure of tricyclocarotol (20) was firmly established by a single crystal x-ray analysis of the ester derivative 22. Selected bond distances and angles of the structure appear in Table 15 and Table 16 while an ORTEP

drawing of the structure appears in Figure 3. It contains no unusual bond distances or angles[47] and is fully consistent with the spectral and chemical data previously discussed. It differs from carotol (1) by the formation of a new bond between C1 and C6 making the rigid tricyclic structure with one seven and two five membered rings as illustrated in Figure 3.

Since tricyclocarotol (20) has a plane positive ORD curve and therefore is optically active, it was surprising to find out that the space group of the crystal was $P2_1/C$ which denotes that the four molecules per unit cell are racemic pairs. For this reason partial racemization must have occurred during the formolysis. In order to determine how this happened, a set of experiments were performed. The results appear in Table 3 of the experimental section. First optically active carotol (1) was treated with 90% formic acid at room temperature for two days. The alcohol 20 and its formate 21 were separated from the other products by silica gel chromatography and reduced with lithium aluminum hydride to give alcohol 20 whose ORD curve was measured. This product 20 was again exposed to 90% formic acid for 12 days. The tricyclocarotol (20) was isolated and its ORD curve measured. In a third experiment, alcohol 20 was reacted for 36 days, separated as before and the ORD curve was measured. All of these experiments gave tricyclocarotol (20) having identical ORD curves (within experimental error). The values on the

Table 15. Tricyclocarotol p-Iodobenzoate (22) Selected Bond Lengths from the Final Refinement

Atoms	Distances, Å
C1-C2	1.544(7)
C2-C3	1.534(8)
C3-C10	1.531(7)
C4-C10	1.528(7)
C4-C5	1.502(9)
C5-C6	1.522(9)
C6-C7	1.541(8)
C7-C8	1.528(8)
C8-C9	1.527(6)
C9-C10	1.547(7)
C1-C9	1.551(6)
C1-C6	1.578(6)

Table 16. Tricyclocarotol p-Iodobenzoate (22) Selected Bond Angles from the Final Refinement

Atoms	Bond Angle, deg
C6-C1-C2	113.8(4)
C6-C1-C9	97.9(3)
C2-C1-C9	103.6(4)
C1-C2-C3	107.1(4)
C2-C3-C10	105.8(5)
C3-C10-C9	102.8(4)
C4-C10-C9	107.3(4)
C10-C4-C5	112.7(5)
C4-C5-C6	113.8(4)
C5-C6-C1	109.1(5)
C5-C6-C7	107.0(5)
C7-C6-C1	103.3(4)
C6-C7-C8	107.4(4)
C7-C8-C9	104.0(4)
C8-C9-C10	115.9(4)
C10-C9-C1	102.5(4)

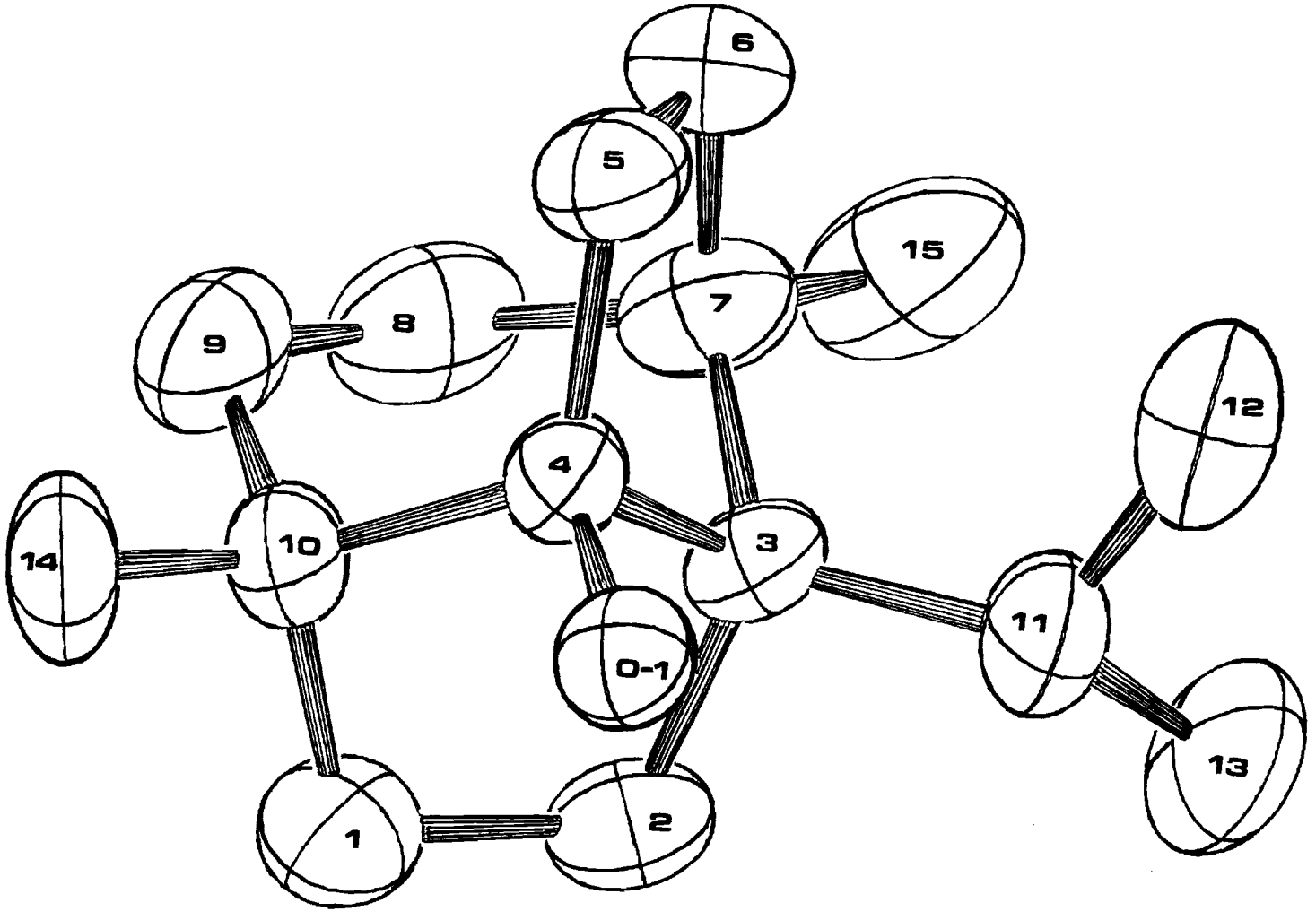


Figure 3. ORTEP of Non-Hydrogen Atoms of Tricyclocarotol p-iodobenzoate 22 with Oxygen Atom Attached to C-9

curve were about half the values of tricyclocarotol (20) recovered in routine formolyses (over 5 days). Therefore, racemization must occur before the formation of the tricyclocarotane compounds 20, 21 since there was no change in the ORDs. In the next experiment, daucene (9) was stirred with 90% formic acid ten days. The alcohol 20 and formate 21 were separated and reduced as above. This time the ORD values were about one third higher than those obtained from carotol (1) formolyses of five or more days. Next, an optically active acoradiene mixture 16 prepared from optically active carotol (1) was exposed to 90% formic acid and tricyclocarotol (20) was isolated as before. This time, however, the alcohol 20 was optically inactive. It is therefore suggested that this product can arise by two pathways, as seen in Figure 4, one which leads from the acoradienes (16) to a racemic mixture of 20 and 21 and the other that leads from daucene (9) to the optically active alcohol 20 and formate 21.

As mentioned above, the alcohol 20 product from the separate formolyses differed in the absolute values of optical rotations as measured by an optical rotatory dispersion spectrometer. The alcohol from the daucene (9) experiment showed the highest rotations. This could mean that daucene went directly to the tricyclocarotane 20, 21 compounds without racemization resulting in the higher rotation values. During the early stages of the formolysis of carotol (1), daucene (9) and the acoradienes (16) are produced. The

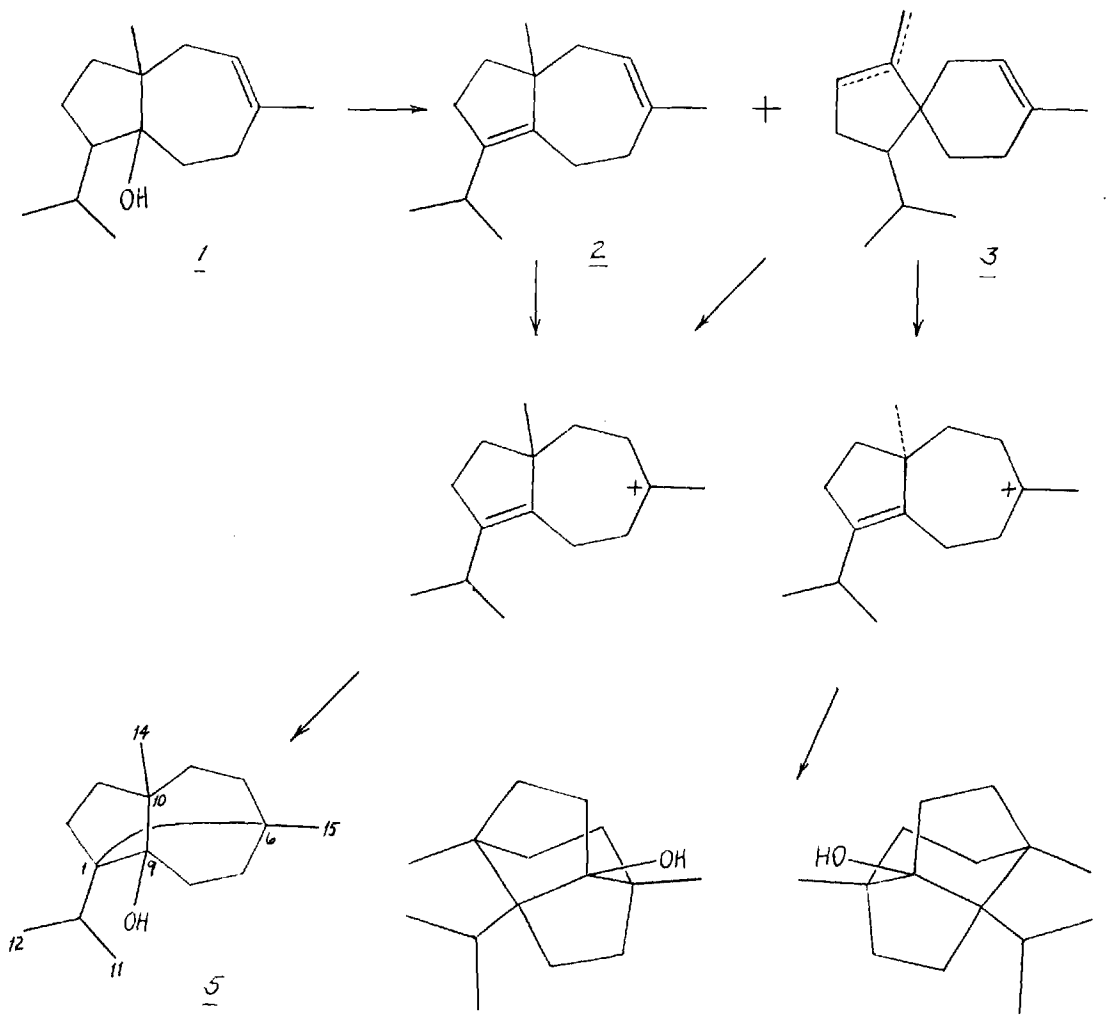
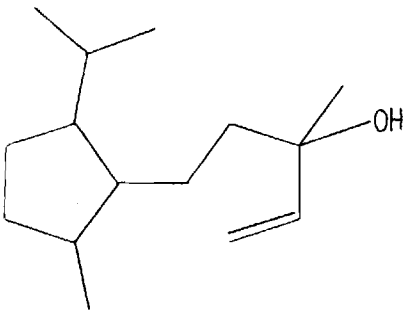


Figure 4. Partial Racemization of Tricyclocarotol (20)

acoradienes (16), as seen from the time studies disappear first. Therefore, it is suggested that when carotol (1) was subjected to acid for two days at room temperature, the acoradienes (16) went into the tricyclocarotane skeleton 20, 21 at a greater rate than daucene (9) making it less optically active than it is when reacted for longer lengths of time. When the same alcohol 20 was returned to the acid and separated again its ORD values did not change which means that only the spiro compounds which can form carbonium ions with subsequent inversion of configuration at the C10 carbon atom can cause racemization. Once the tricyclic compounds are formed they do not reversibly go to the acoradienes (16).

This is substantiated by the fact that Clower[24] returned the products from the formolysis back to acid at room temperature and checked the reactions by glc. In no case did he find acoradienes (16). However daucene (2) was present in varying amounts for the first days of the formolysis of tricyclocarotol (20) and its formate (21).

The conversion of the acoradienes (16) to carotane compounds by an acid catalyzed rearrangement is significant biogenetically as it shows that the two skeletons can be interconverted. It has already been noted that the spiro compounds can be made from carotol (1).[24,45] Both the acorane (16) and daucane (2) skeletons have been synthesized from the same alcoholic precursor 35.[48]



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It would be interesting to measure the extent of racemization. For this purpose, optically active shift reagents [Eu and Pr tris-[3-(trifluoro-methylhydroxymethylene)-d-camphorato] were added to tricyclocarotol (20) from a five day formolysis. It was expected that the diastereomers would complex with the shift reagents differently giving two sets of signals in the proton NMR spectrum. With the methyls differentiated, the relative amounts of each enantiomer could be determined by integration. Unfortunately, these shift reagents did not cause any separation.

As mentioned in the discussion of the formolysis time study, from 20 hours at 45°C, the olefin 17, 18 mixture is the predominant product with tricyclodaucene (17) being the major constituent up to 40 hours of the reaction time. After separating the olefins 17, 18 from the other products by silica gel chromatography, they were separated from each other by further chromatography on silica gel impregnated with silver nitrate (25%). Tricyclodaucene (17) was eluted first with distilled olefin free petroleum ether.

According to the infrared spectrum with an absorbancy

at 810 cm^{-1}, the olefin 17 was trisubstituted. The ^{1}H-NMR also had a signal (δ5.07) for one olefinic proton along with two methyl doublets (δ0.72, 0.90) for the isopropyl group, one quaternary methyl (δ1.00) and a multiplet for the olefinic methyl (δ1.62). In the off resonance decoupled ^{13}C-NMR there was also a singlet (δ142.4) for the disubstituted olefinic carbon (C7) and a doublet (δ116.2) for the olefinic carbon with one proton (C6).* Using the rules on substituent effects in Strother's book, the one signal for the quaternary carbon was assigned to (C3) once the structure was verified.[46] The mass spectrum which will be discussed later showed a molecular ion at m/e 204 (35%) and a strong one at m/e 161 (27%) for the loss of an isopropyl ($M^{+}-C_3H_7$). It also had a plane positive ORD curve, although since it is derived from tricyclocarotol (20) it also must be a racemic mixture. All of these results along with the carbon and hydrogen analysis substantiate the proof that tricyclodaucene (17) is a tricyclic trisubstituted optically active olefin containing two methyl groups on an isopropyl, one on a quaternary carbon and one on an olefinic carbon. For further structural elucidation the reactions which are summarized on Figure 5 were performed.

An attempt to make the trisubstituted epoxide 24 was first made by reacting m-chloroperbenzoic acid with the olefin 17 in a homogeneous methylene chloride solution. The product

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*Numbering for this structure on Figure 5.

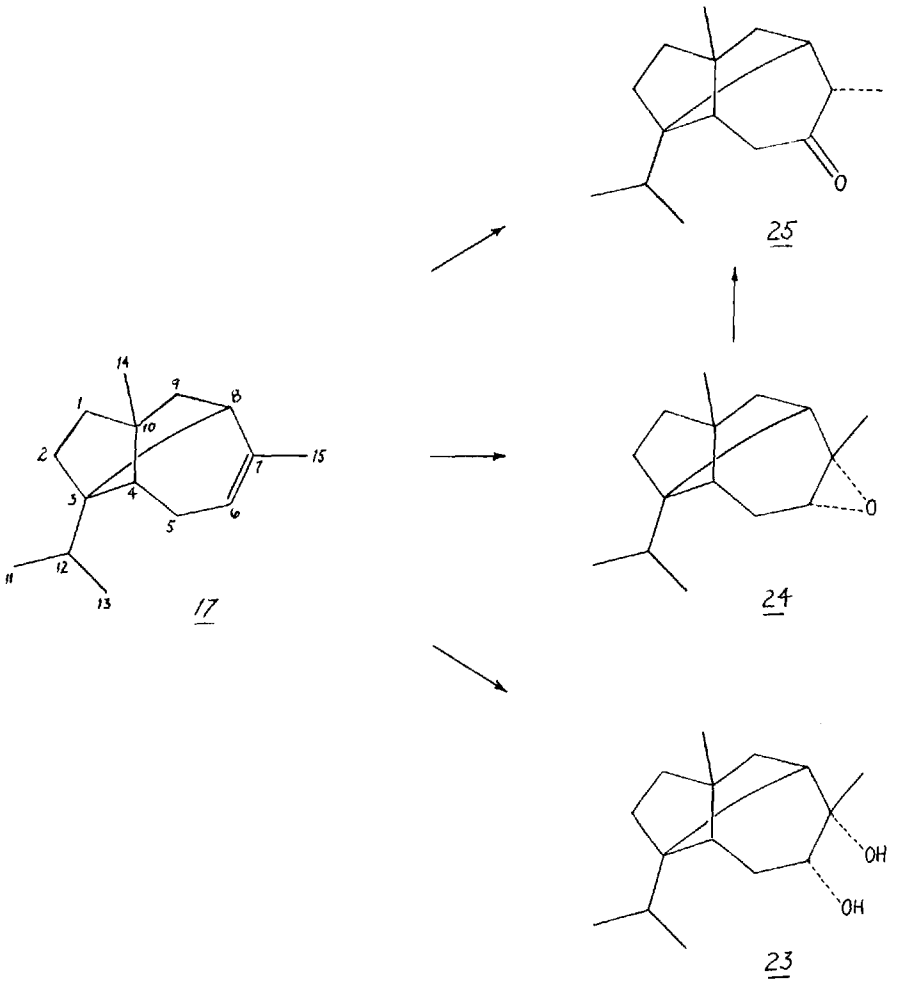
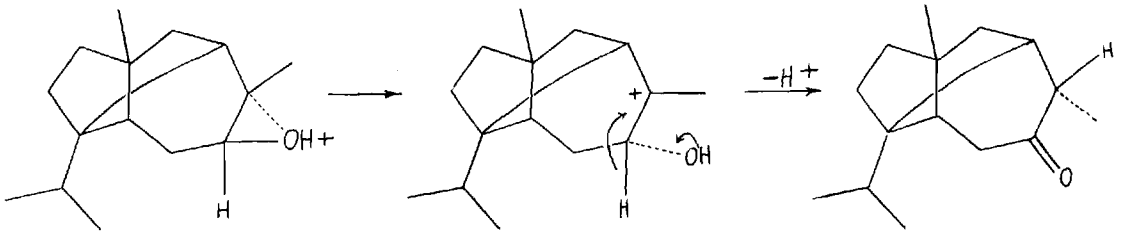


Figure 5. Reactions of Tricyclodaucene (17)

was a semi-solid which was pure by glc analysis. However there was a carbonyl absorbancy (1710 cm^{-1}) in the IR and 3 methyl doublets (δ0.90, 0.93, 1.01) the third coming from (C15)$\underline{H}_3$ along with a methyl singlet (δ0.98) and a doublet (δ2.33) integrating for one proton for the (C7)$\underline{H}$ next to the carbonyl. An exact mass determination for the molecular ion gave m/e 220.188 which corresponds to the molecular weight (220.183) for the formula $C_{15}H_{24}O$. This was confirmed by the carbon and hydrogen analysis of the 2,4-dinitrophenyl-hydrazone derivative.

This information was consistent with the assigned structure for the ketone 25 which was formed by the acid catalyzed or pinacol rearrangement of the tricyclic epoxide 24 as illustrated below. The epoxide 24 was formed on the least hindered side of the molecule. It then opened with subsequent migration of a hydride to invert the methyl.



In retrospect this result would not be surprising since mineral acids are often used to convert an olefin into a carbonyl by way of an epoxide.[49] With the rigid skeleton of the tricyclic epoxide 24 in this case it is not surprising

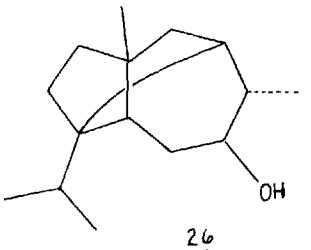
that small amounts of acid would easily cause epoxide 24 to rearrange.

It was finally successfully prepared by using m-chloroperbenzoic acid in a biphasic system with aqueous sodium bicarbonate in the aqueous phase.[30] The ^{1}H-NMR spectrum looked like pure epoxide with two methyl singlets (δ0.95, 1.32), one more downfield (C15)$\underline{H}_3$ since it is next to the epoxide and one methyl doublet (δ0.90) for those on the isopropyl. However there were 25 signals on the ^{13}C-NMR one of them at δ212.3 for a carbonyl and two for the epoxide carbons at δ153.3 and 110.8 indicating that some rearrangement had occurred. Chromatography of the epoxide 24 on neutral alumina also resulted in the tricyclic ketone 25.

When attempts were made to ozonize the olefin 17 to cleave the double bond to determine its placement, work up of the ozonide by either zinc in acetic acid or hydrogen peroxide also resulted in the ketone 25. The ozonide would open according to a mechanism similar to that for the epoxide 24 by acid catalysis. Attempts were made to obtain a crystal of the 2,4-dinitrophenylhydrazone for x-ray analysis. Slow growth of crystals in an isopropanol atmosphere from an isopropanol-chloroform mixture gave orange needles; but when these were put on the diffractometer they were found to be twinned. The 5-iodo-2-nitrophenylhydrazone derivative was prepared; however, it was not obtained in crystalline form.

In further attempts to elucidate the structure of

tricyclodaucene (17), the ketone 25 was reduced with lithium aluminum hydride to give a secondary alcohol 26 resulting from reduction on the least hindered side with absorbancy at 3400 cm^{-1} in the infrared and an ^{1}H-NMR spectrum with three methyl doublets (δ0.88, 0.92, 1.10) one methyl singlet (δ1.10) and a singlet (δ3.81) for (C6)H. Reduction of the epoxide 24 with lithium aluminum hydride gave starting material plus the secondary alcohol 27, as major products which were separated by chromatography on deactivated basic



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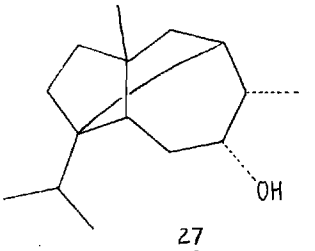

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alumina. This product also had 3 methyl doublets (δ0.83, 0.87, 1.02), one methyl singlet (δ1.10) for (C14)H_3 and a singlet (δ3.83) for (C6)H and OH absorbancy (3400 cm^{-1}) in the IR. With the assumption that both reductions occur from the least hindered side of the molecule the fact that two different secondary alcohols formed with similar ^{1}H-NMR spectra would verify the mode of the rearrangement of the epoxide 24 by hydride ion migration followed by inversion of the methyl at C7.

With the spectral evidence of tricyclodaucene (17) and

its derivatives at hand, many aspects of its structure were still unclear, that is the exact placement of the new bridging bond and the double bond. Since tricyclocarotol (20) formed without skeletal rearrangement, and can be converted to the olefins 17, 18, it was assumed that this tricyclic skeleton formed in a similar way. With the five-seven membered ring system in tact and knowing that at least one qartenary carbon (C14) was present along with an olefinic methyl (C15), the double bond could go either from C6 to C7 or from C7 to C8. If it went to C8, the bridge could be formed to join C6 to C1 or C2. Models show that these structures would be very strained though. With the double bond at C6 to C7, the bridge could go from C8 to C2 or C3. As these results were inconclusive, it was still necessary to make a derivative for x-ray analysis.

An attempt to make a diol 23 from potassium permanganate and sodium metaperiodate[31] resulted in a mixture as seen by glc analysis with an infrared containing absorbancies for hydroxyls as well as carbonyls. Next the olefin 17 was reacted with osmium tetroxide in dry pyridine[29] to produce after chromatography on deactivated alumina and crystallization from pentane pure diol 23 in the form of long white needles. The infrared with absorbancies at 3400 and 1050 cm^{-1} were consistent for an alcohol. While the ^{1}H-NMR agreed with the structural features described above with two methyl doublets (δ0.83, 0.90) for those of the isopropyl,

two methyl singlets (δ1.00, 1.33) and a triplet for the C7 proton. The diol 23 was also optically active as seen by a plane positive ORD curve. In the mass spectrum there was no molecular ion but a prominant ion m/e 220 (29%) corresponding to loss of water.

The structure of tricyclodaucene (17) was firmly established by a single crystal analysis of the diol 23. Selected bond distances and angles in Tables 17 and 18 while an ORTEP drawing appears in Figure 6. It contains no unusual bond distances or angles[47] and is consistent with the spectral and chemical data discussed. It differs from carotol (1) by the formation of a new bond between C3 and C8 making the rigid tricyclic structure with one seven, six and five membered rings as illustrated in Figure 6.

The conditions of the formolysis were changed according to the product that was desired. An explanation of the time study that follows will clarify this. When tricyclocarotol (20) or tricyclodaucene (17) were desired, the reaction was ordinarily conducted at 25°C for five days. The yields of olefins 17, 18 attained were very low from the chromatography on silver nitrate impregnated silica gel so the conditions that were chosen, six days at 45°C, gave the tetrasubstituted olefin 18 pure enough to be used for reactions after chromatography on silica gel.

The infrared spectrum for pure olefin 18 did not contain any absorptions indicative of functional groups,

Table 17. Diol 23 Selected Bond Distances from the Final Refinement

Bonds	Distances, Å
C1-C2	1.49(2)
C2-C3	1.61(2)
C3-C4	1.61(1)
C4-C5	1.55(1)
C5-C6	1.48(2)
C6-C7	1.54(1)
C7-C8	1.54(1)
C8-C9	1.58(1)
C9-C10	1.55(2)
C1-C10	1.55(2)
C3-C8	1.57(1)
C4-C10	1.54(1)

Table 18. Diol 23 Selected Bond Angles from the Final Refinement

Bonds	Angles, in degrees
C10-C1-C2	104(1)
C1-C2-C3	103(1)
C2-C3-C4	102.2(3)
C2-C3-C8	106.0(8)
C4-C3-C8	96.8(8)
C3-C4-C10	93.9(8)
C3-C4-C5	112.5(9)
C4-C5-C6	117.4(9)
C5-C6-C7	114.9(9)
C5-C10-C4	114.0(8)
C6-C7-C8	111.8(8)
C7-C8-C3	111.9(8)
C7-C8-C9	112.5(8)
C9-C8-C3	103.2(8)
C8-C9-C10	102.8(9)
C9-C14-C4	103.6(9)
C1-C10-C4	101.0(9)
C2-C3-C8	106.1(8)
C10-C4-C5	114.0(8)
C7-C8-C9	112.5(8)

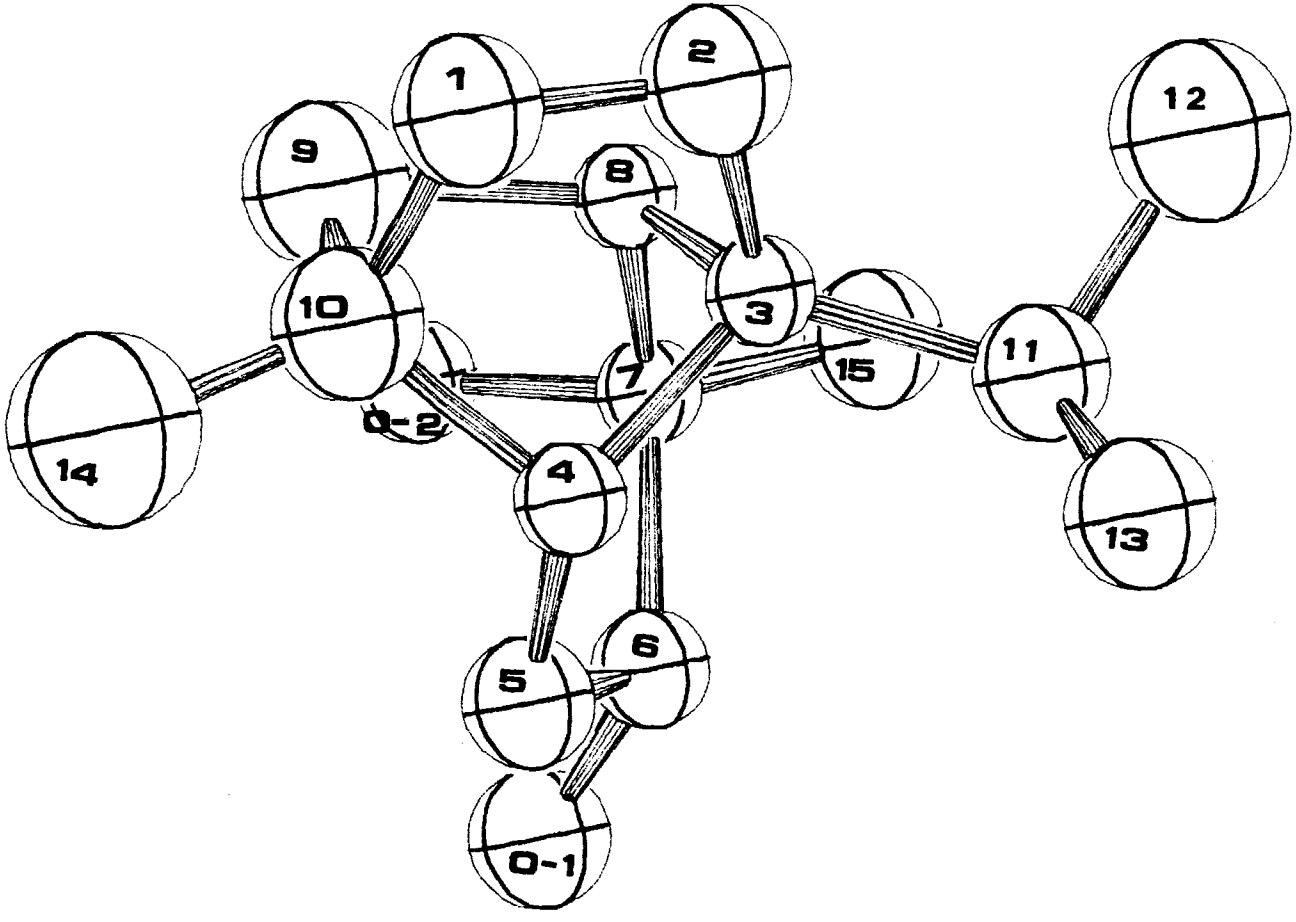


Figure 6. ORTEP of Non-hydrogen Atoms of Diol 23 (Mirror Image)

While the ^{1}H-NMR contained two methyl singlets (δ0.86, 0.98) in the alkyl range, one methyl singlet (δ1.58) and one doublet (δ1.62, J 1 Hz) for methyls attached to olefinic carbons and two broad signals (δ2.28, 2.76) integrating for one proton each for protons next to the olefinic carbon. When the signal at 137.0 Hz was irradiated the doublet at δ1.62 collapsed to a singlet, while the signal (δ1.62) remained a doublet when irradiated at 165.5 Hz. This would be indicative of homoallylic coupling with one proton on the same side as the methyl (δ1.62). In the ^{13}C off resonance decoupled NMR there were two singlets for olefinic carbons, δ141.9 (C3) and 118.0 (C11) and two singlets for quartenary carbons, δ41.9 (C7) and 32.6 (C10) as the only discernible signals.[46] In the mass spectrum the base peak is the molecular ion at m/e 204 ($C_{15}H_{24}$) indicating a stable compound and confirming the fact that the isopropyl contains the double bond (no M^{+}-C_3H_7 fragment). More discussion on the mass spectrum will follow in another section. A plain positive ORD curve was attained implying optical activity. Partial racemization, though, is expected from the racemization caused by the acoradienes (16). This spectral data along with a carbon and hydrogen analysis indicated that isotricyclodaucene (18) was an optically active tricyclic tetrasubstituted olefin with the isopropyl group containing the olefinic moiety. From the ^{1}H-NMR it was also suspected that there was one proton on each of the carbons next to the olefinic

group. There were also methyls on both of the quaternary carbons as shown by ^{1}H-NMR.

As with tricyclodaucene (17) a diol 27 was prepared with osmium tetroxide in dry pyridine after an attempt with potassium permanganate and sodium metaperiodate failed. The crude diol 27 was chromatographed on deactivated alumina repeatedly to remove the purple color. Crystallization continually resulted in a white powder (mp 86-88°C) and finally colorless needles (mp 68-69°C). Carbon and hydrogen analyses of both solids did not agree with expected values, although both had the same spectral properties and one peak by glc. IR absorptions included 3500 and 1175 cm^{-1} for the hydroxyls, while the ^{1}H-NMR contained four methyl singlets (δ0.89, 1.07, 1.20, 1.26) in agreement with the olefin's 18 spectrum. Characteristic of alcohols there was no molecular ion but a base peak at m/e 177 (M^+-H_2O-C_3H_7) in the mass spectrum.

An x-ray analysis of one of the colorless crystals resulted in a decrease of more than 8% of the integrated intensities of the test reflections within 17 hours of data collection. Coating the crystal with epoxy did not inhibit decomposition. This result along with the difficulty in attaining a reasonable analysis could be from the trapping of solvent molecules during crystallization.

At this point the chemical degradation of the molecule was begun.* The tricyclic pentanone 28 was prepared from the

*This is illustrated in Figure 7.

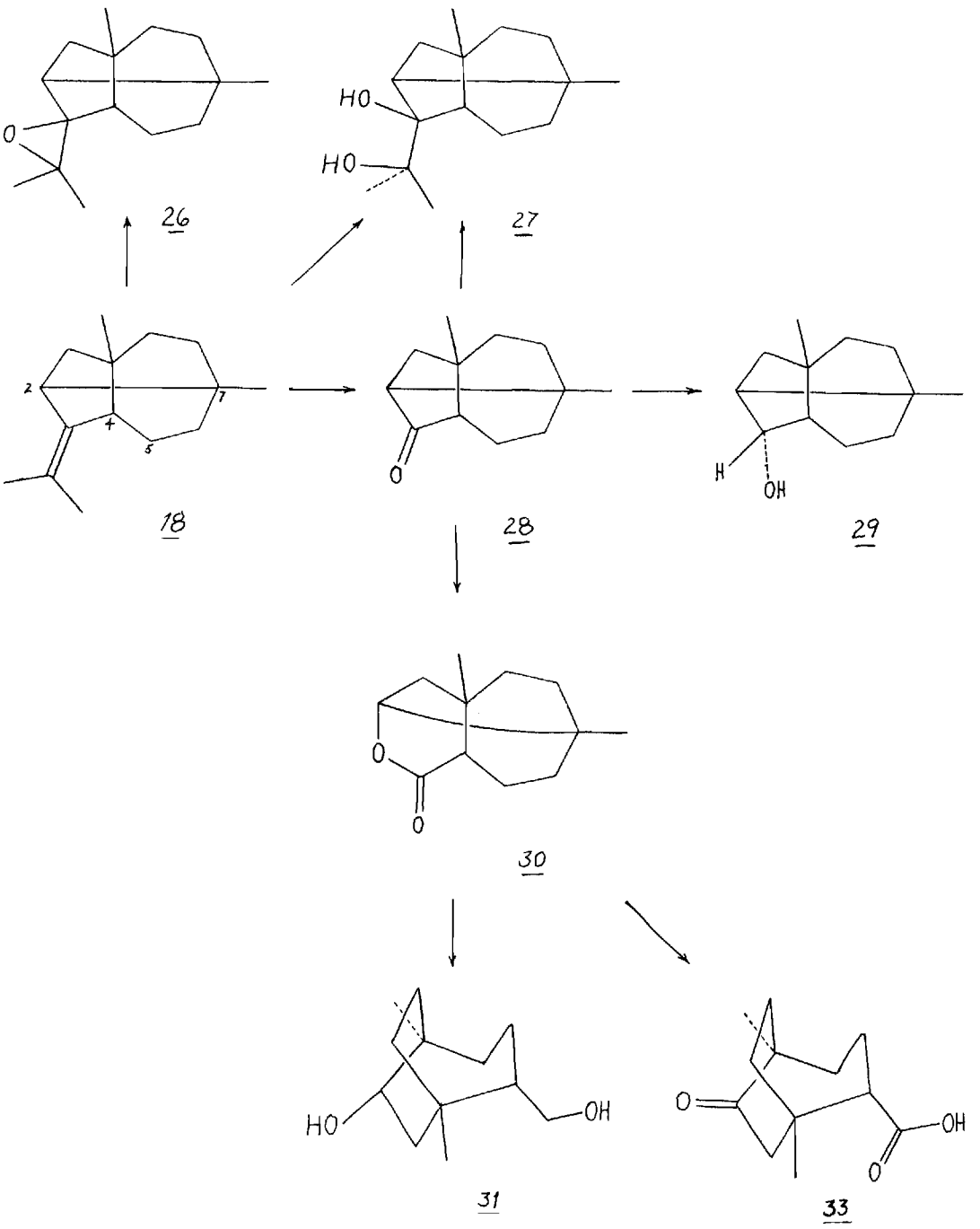


Figure 7. Reactions of Isotricyclodaucene (18)

diol 27 with lead tetraacetate; but because of the low yields of the two reactions, ozonolysis with reductive work-up was more successful. After chromatography on deactivated alumina, the ketone 28 was obtained as a white semi-solid. The IR had a carbonyl absorption at 1745 cm^{-1} confirming the fact that the isopropyl had been attached to a five membered ring. Two methyl singlets (δ0.97, 1.05) and broad signals (δ1.98, 2.46) integrating for one proton a piece were present in the ^{1}H-NMR, while the following signals for five carbons were discernible in the off resonance decoupled ^{13}C-NMR spectrum: δ 217.2 (C=O), 51.5 (d, H-C-C=O), 47.3 (H-C-C=O), 42.3 (s) and 35.8 (s, quartenary). As a good model compound could not be found assignments of these peaks were not made. An exact mass of the molecular ion m/e 178.132 (66%) plus a carbon and hydrogen analysis of the 2,4-dinitrophenylhydrazone derivative confirmed the fact that this molecule was a tricyclic ketone 28 ($C_{12}H_{18}O$) resulting from the loss of the isopropyl on the olefin 18.

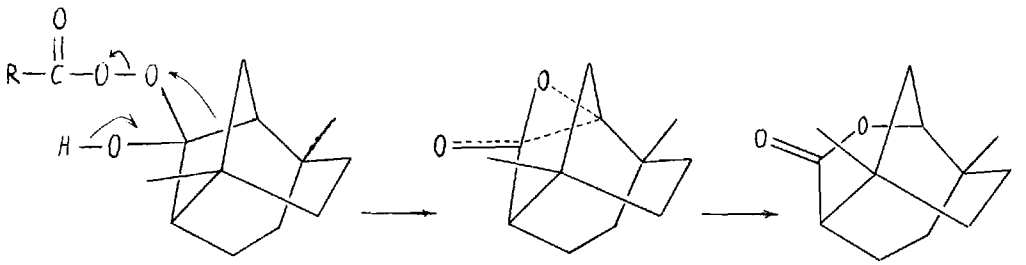
With this evidence it appears that the structure contains one five membered ring, two quartenary carbons (both with methyls) and carbons bearing one proton apiece flanking the carbonyl. The structure as indicated on Figure 7 with the new bond between C7 and C2 would be consistent with this data. Since the tricyclocarotane (20) and tricyclodaucene (17) structures were found to form with retention of the daucane (2) (5-7 membered ring) carbon skeleton, it is believed

that the tetra-substituted olefin 18 is similarly derived. No other structure from this skeleton would fit the data attained so far. In order to ascertain this additional reactions were done.

Reduction of the tricyclopentanone 28 with lithium aluminum hydride gave a secondary alcohol 29 with typical hydroxyl absorptions (3600, 3450 cm^{-1}) in the IR. While the ^{1}H-NMR in addition to two methyl singlets (δ0.88, 0.93) contained a doublet of doublets (δ4.23, J 8, 5 Hz) for the proton on the same carbon as the hydroxyl. This would mean that the (C3)H is on the same side of the molecule as C14 with a dihedral angle of about 0° with (C4)H which agrees with J 8 Hz and a dihedral angle of about 40° with (C2)H for J 5 Hz. A model of this compound does have those angles in agreement. The base peak m/e 107 is a fragment typical of these daucane (2) and tricyclic compounds, while there is a fragment m/e 162 (98%) for M^+-H_2O. Since the reduction proceeded from the less hindered side of the molecule, the hydroxyl is hindered. This was also seen by the recovery of alcohol 29 when attempting to make the p-iodobenzoate derivative.

A Baeyer-Villager oxidation was next performed with the ketone 28 and m-chloroperbenzoic acid to continue the sequence on Figure 7. As seen by glc only one lactone 30 was obtained as the product. In order to predict which of the two possible lactones had been formed, a model of the ketone

was built. If the peracid reacted with the carbonyl from the less hindered side of the molecule as indicated below, then migration would occur through the energetically



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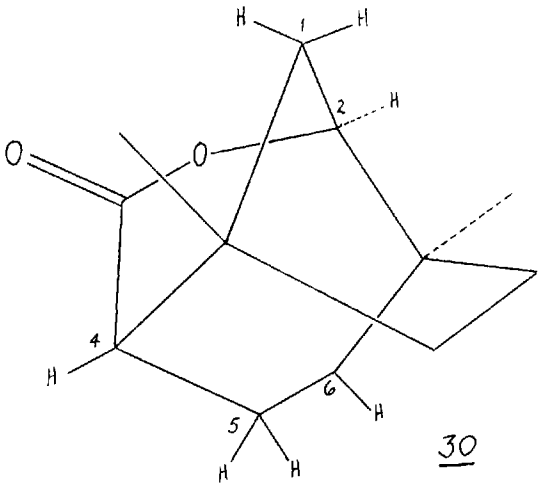
favored chairlike transition state to give the lactone (30).[52] The proof that this was the product came from the 100 mHz ^{1}H-NMR. The expected signals (δ0.98, 1.09) for the methyls on quaternary carbons were present in addition to a triplet of doublets (δ2.80, J 4.8, 1.6 Hz) for the (C4)H next to the carbonyl and a triplet (δ4.42, J 1.7 Hz) for the (C2)H next to the oxygen. The higher field signal (δ2.80 triplet of doublets) is due to coupling of $(C5)H_2$ with (C4)H to give J 1.7 Hz which is in close agreement with the coupling constant for a dihedral angle of 60° and one (C6)H with (C4)H to give J 4.8 Hz is in agreement for the coupling constant due to long range coupling of protons in a rigid structure having a "W" conformation as seen below. Since there is a quaternary carbon next to C1 this type of coupling would



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not be expected if migration had occurred in the other direction. The lower field triplet (δ4.40) with its coupling constant (J 1.7 Hz) fits the model with a dihedral angle of 60°.

Crystallization of an analytical sample gave white flakes (mp 63-64°C) with a carbon and hydrogen analysis in agreement with the molecular formula ($C_{12}H_{18}O_2$). There was no molecular ion in the mass spectrum while the characteristic fragment m/e 107 was the base peak. Absorptions in the IR (1750, 1250, 1140, 1050 cm^{-1}) were typical for a six membered lactone. All of this data is consistent with the chosen tricyclic skeleton.

To continue the degradation the first approach that was taken was to open the lactone 30 and oxidize the resulting alcohol to give 33. The choice of conditions for this are important since the tendency for the opened carboxylic acid and alcohol is to reform the lactone. A method by Gopal which prevents this was chosen using oxidation with ruthenium tetroxide.[42] Although the reaction proceeded as described, the black color from the ruthenium persisted and

the yield was very low.

The lactone 30 was cleanly opened by reduction with lithium aluminum hydride to the 1,5-dimethyl-[3-2-2]-bicyclononane skeleton 31 which is unusual.[50] Its IR had absorptions at 3610 and 3425 cm^{-1} for the hydroxyls. The carbon and hydrogen analysis agreed with the molecular formula $C_{10}H_{22}O_2$ as did the mass spectrum with no molecular ion, m/e 180 (9%, M^+-water) and a base peak at m/e 139. While the ^{1}H-NMR was as expected for the product of the lactone 30 with methyl singlets (δ0.92, 1.02), a doublet (J 5 Hz) for (C3)$\underline{H}_2$ at δ 3.46 and a doublet of doublets (J 5, 10 Hz) for (C2)$\underline{H}$ at δ 3.18, the coupling constants are in agreement for those of hydrogens with dihedral angles of 10° (J 10 Hz) and 40° (J 5 Hz). This product is a [3-2-2]-bicyclononanol 31 with two bridgehead methyls. One of the hydroxyls is attached to the ring at C6 and is next to a secondary carbon while the other is on a methylene substituent at C2.

Long white needles with a sharp melt (110-111°C) were obtained from crystallization from ether-ethyl acetate. However, they were found to be twinned when put on the diffractometer.

Assuming that the five-seven membered ring of the daucane skeleton 2 is intact, the results from these products substantiate the previous results. In summary isotricyclo-daucane (18) consists of one five, six and seven membered rings with two bridgehead methyls. It contains an exocyclic

olefinic isopropyl group flanked by a proton on each side. Therefore the new bond that is formed joins C2 and C7. These conclusions agree with the structure as presented.

During the course of the degradation of the molecule, attempts were made to obtain a solid derivative for x-ray analysis. Every compound that was made was a solid but none were in a good enough form for x-ray analysis although some were actually put on the diffractometer. Several were made from the tricyclic ketone 28 including the 2,4-dinitrophenyl-hydrazone, semicarbazone and p-iodocarbonylhydrazone which were fully characterized. All had absorptions at about 3300-3500 cm^{-1} for NH and 1640-1680 cm^{-1} for C = N as did the 5-iodo-2-nitrophenylhydrazone and p-bromosulfonyl hydrazone. The ^{1}H-NMR's had highfield methyl signals that were in close agreement to each other, in addition to signals characteristic of their individual phenyl substitutions. The mass spectra of the 2,4-dinitrophenylhydrazone, semicarbazone and 2,4-dinitrophenylhydrazone contained fragments that were typical of the ketone 28. The semicarbazone and p-iodocarbonylhydrazone gave white flocular solids upon repeated crystallizations from varied solvent systems, while the p-bromosulfonyl hydrazone, 2,4-dinitrophenyl-hydrazone and 5-iodo-2-nitrophenyl-hydrazone all gave ostensibly nicely formed crystals. Unfortunately, all were found to be twinned when put on the diffractometer. The only reason that can be made for the inability to get a good crystal with all of these attempts is that several different conformational forms were present

first from the partially racemized product and then from the syn and anti derivatives which inhibited good molecular stacking.

Earlier in the work an epoxide 26 was synthesized, but this turned out to be an oil. It was made from a mixture of olefins 17 and 18 in a biphasic system as described before and were easily separated on deactivated alumina. The product 26 with a plane positive ORD cure was optically active. The IR had absorptions at 1150, 1110 and 850 cm^{-1} for a tetrasubstituted epoxide. While the ^{1}H-NMR was in accord with the structure with two methyl singlets (δ0.93, 1.05) for the ones on quartenary carbons and two downfield (δ1.32, 1.36) for those on the epoxide. On the ^{13}C-NMR with off resonance decoupling the following singlets δ 77.2 and 61.6 for epoxide carbons and δ 47.6 and 39.9 for quartenary carbons were discernible. A molecular ion at m/e 220 (5%) and base peak at m/e 177 ($M^{+} - C_3H_7$) along with elemental analysis suggests the molecular formula ($C_{15}H_{24}O$).

The most current derivative made for x-ray analysis was the primary p-iodopenzoate of the 1,5-dimethyl-[3-2-2]-bicyclononanol 32. It was a solid but a suitable crystal for x-ray analysis was not obtained.

In order to determine the mechanistic relationships among the products formed during the formolysis of carotol (1) a time study of the reaction at 45°C was performed. Small amounts of carotol (1) were stirred in 90% formic acid

for designated times, then the reaction was quenched by the addition of saturated salt solution which was extracted with ether. These extracts were analyzed by glc and relative amounts of product were determined by measurement of peak areas.

As has been mentioned earlier, Clower had done some time studies of the reaction at room temperature.[24] However he measured the amounts of products with glc by directly injecting the formolysis mixture into the gas chromatograph. As this mixture was not homogeneous, it was found that the amount of material varied per injection depending upon where in the mixture the sample was drawn. Therefore in these experiments extractions were done as described. Also by examining the results at this elevated temperature, it is seen that the reactions he studied at room temperature had not approached equilibrium.

During the first few minutes of the reaction, as illustrated in Figure 8,* carotol (1) is dehydrated to a mixture of daucene (9) (85%) and acoradienes (16) (15%) by 20 minutes. These products were also found by other workers.[1,27] Within four hours, the acoradienes (16) have been converted to other products; while the amount of daucene (9) has reached a plateau. As these dienes disappear the proportion of the products from the tricyclocarotol skeleton

*The data for these figures are on Tables 5, 6 and 8 of the experimental section.

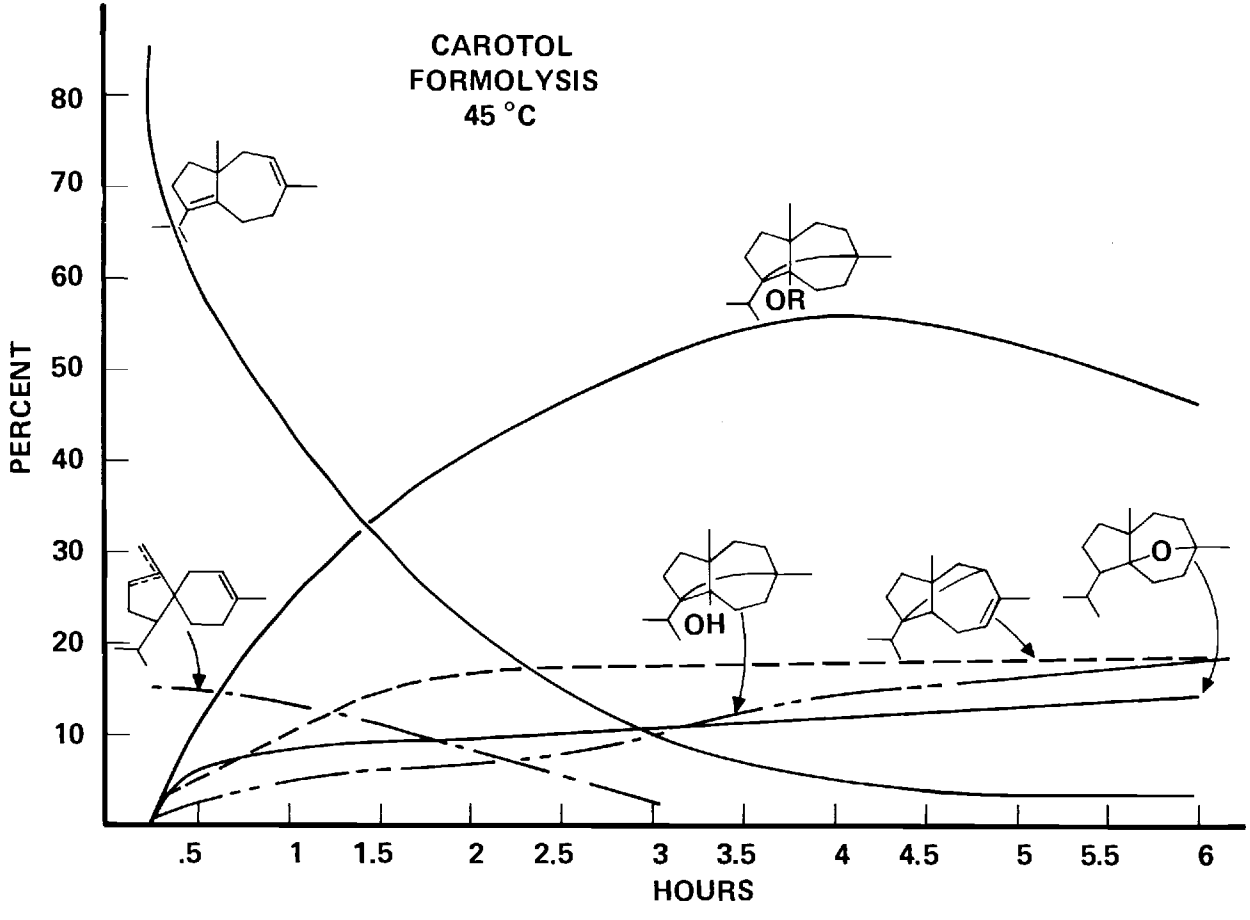


Figure 8. Major Products During First Six Hours

20, 21 are increasing, with the formate 21 in excess. The formate 21 decreases as it is hydrolyzed to alcohol 20. The amount of tricyclic olefins 17, 18 and the ether 19 are also increasing but at a slower rate.

Figure 9 shows the major formolysis products obtained from 24 to 144 hours of reaction time. From 24 to about 90 hours all of the products are at a plateau. Then the alcohol 20, formate 21 and ether 19 decrease to the end of the study, 144 hours. At the same time the amount of olefins 17, 18 rises sharply approaching 100% as illustrated. The proportion of ether does not vary much for the study. It rises to a maximum of 23% at 24 hours and starts dropping to 10% at 72 hours where it remains for the duration of the study. During the course of the reaction, as seen in Table 7 of the experimental section, the amount of volatile unknowns which were minor products varied from about 10 to 15%.

Another observation that was made was that the ratio of olefins 17, 18 to each other also changed during the formolysis as seen on Figure 10. In the very early stages only tricyclodaucene (17) was present. As the reaction progressed the ratio of isotricyclodaucene (18) increased. Within 40 to 50 hours, there were equal amounts of the two. By six days only 20% of the olefin mixture was tricyclodaucene

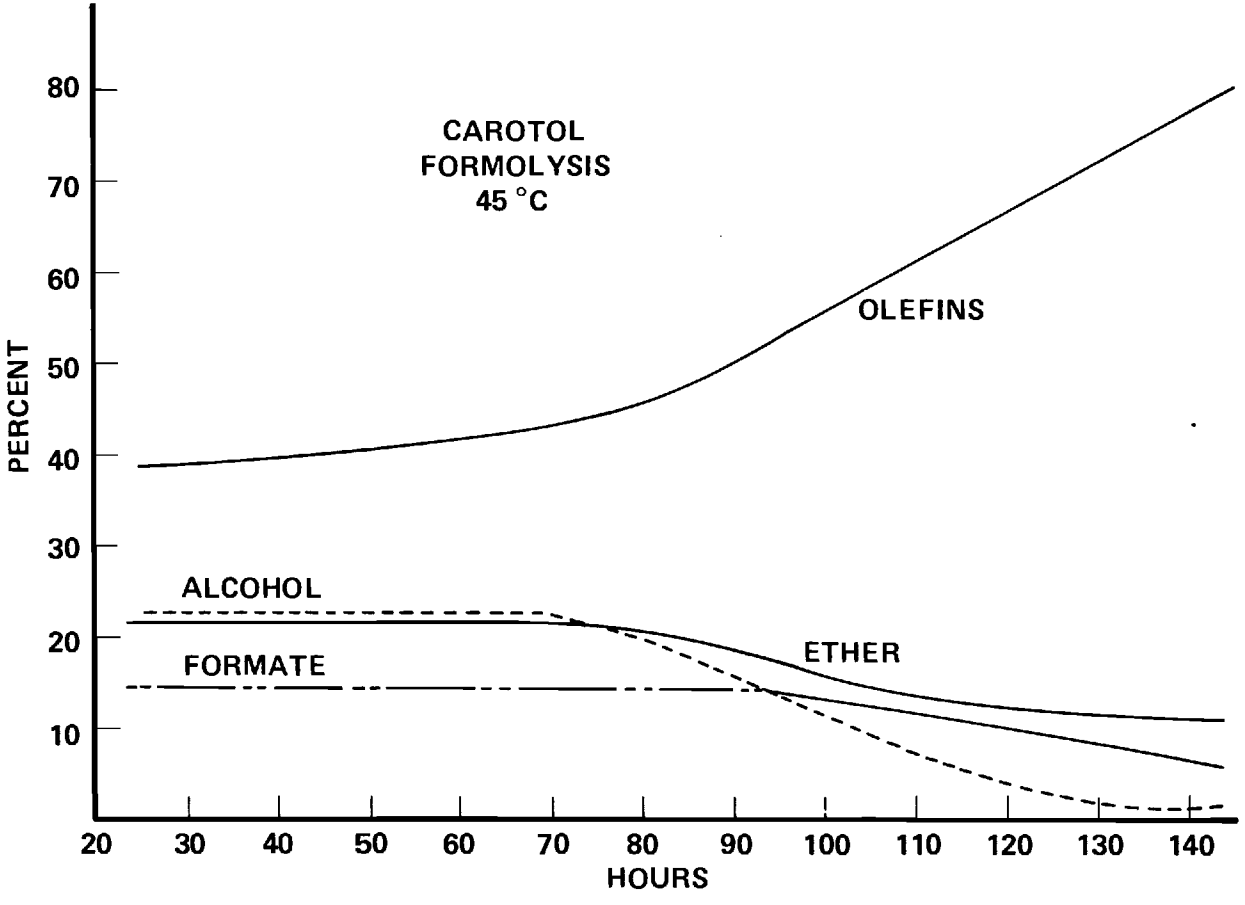


Figure 9. Major Products from 24 to 144 Hours

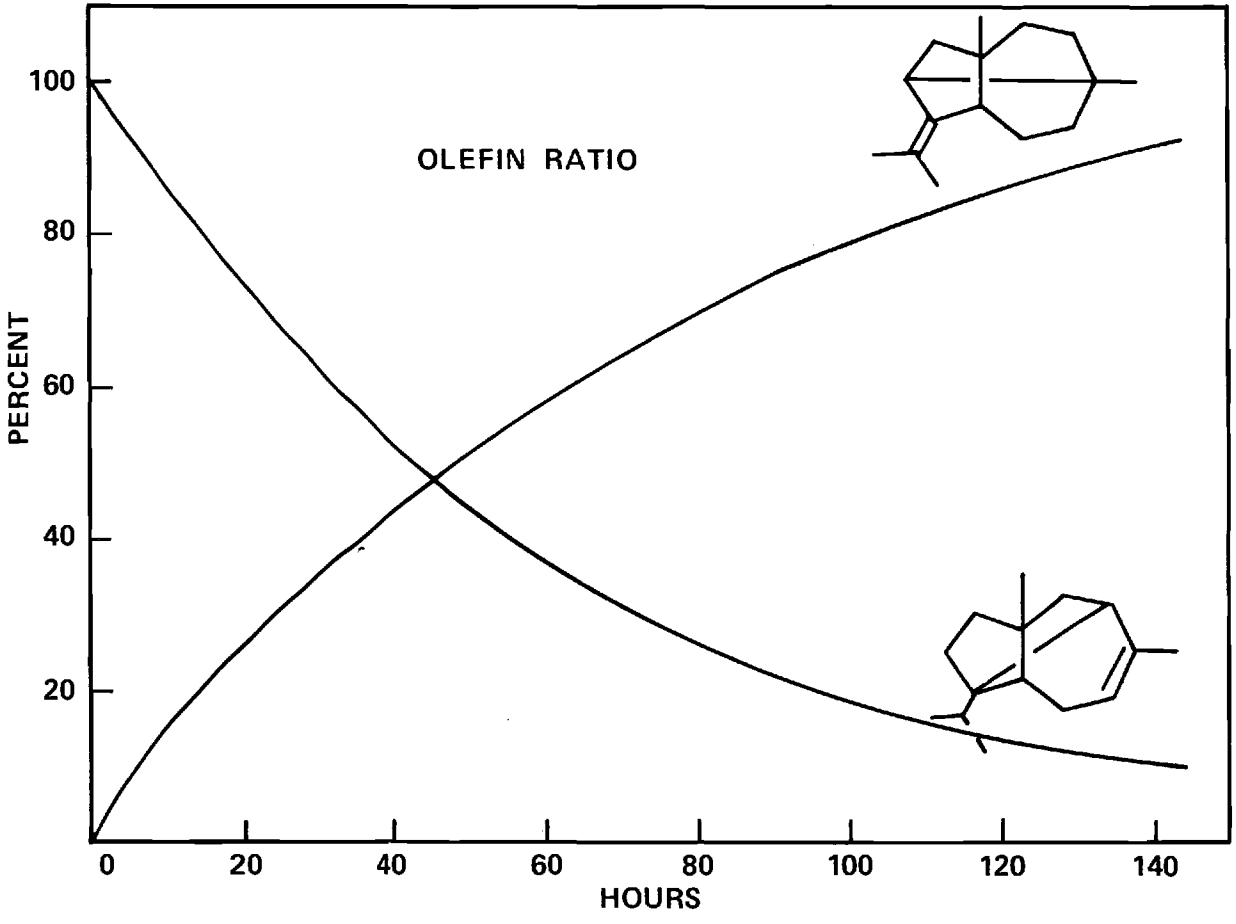


Figure 10. Carotol Formolysis, 45°C Olefin Ratio

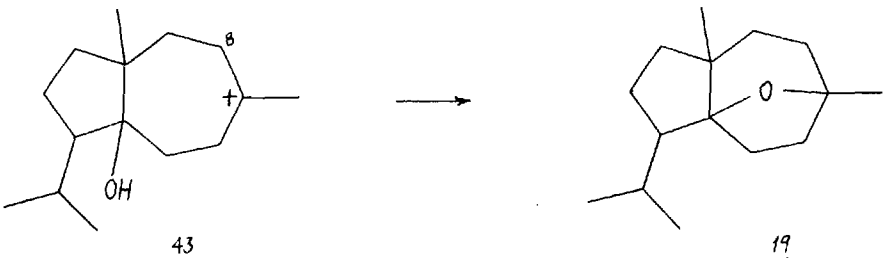
(17) and the rest was isotricyclodaucene (18). Since the olefin mixture is the major product as the reaction approaches equilibrium, that would mean that isotricyclodaucene (18) is thermodynamically the most stable product of the tricyclic compounds while the tricyclocarotol formate (21) is kinetically favored.

Similar trends are seen in the data on Table 2 of the experimental section for the reaction at 25°C. The amount of olefins 17, 18 is steadily increasing to 42 days, the ether 19 slowly increases and is starting to decrease during this time and the tricyclocarotane products 20, 21 are decreasing steadily from 5 to 42 days.

These results are in accord with several observations that Clower made in his formolysis studies conducted at 25°C.[24] In submitting daucene (9) to formolysis for ten days he obtained a mixture consisting of the normal rearranged products. Both the alcohol 20 and formate 21 gave the same product composition after 11 days; while the formolysis of tricyclocarotol 17 for 12 days gave a mixture of tricyclodaucene (17) (58%) and isotricyclodaucene (18) (41%) with a trace of alcohol 20 (1%). Whereas daucane ether (19) after 12 days did not react much. Its mixture contained ether 19 (69%), combined olefins 17, 18 (2%) and tricyclocarotanes 20, 21 (28%).

With all of these results considered, the following mechanism on Figures 4 and 11 is postulated for the formation

and interconversion of the formolysis products of carotol (1). As mentioned in the discussion on the partial racemization of products, the acoradienes (16) which are present during the first stage of formolysis racemize to the daucene carbonium ion 36, 37 which are enantiomeric, by protonation then migration of one of the bonds on the spiro carbon to yield either the ion 36 with the same conformation as daucene (9) or ion 37 with the inverted methyl, its mirror image. For clarity only the ions and their products with the conformation of carotol (1) are presented in Figure 11. Since the ether 19 is produced in the beginning, remains at a steady ratio with respect to the other products and the other products are not converted to it, it must arise from protonation at C8 before dehydration followed by the reaction of the oxygen with the carbonium ion 43 and subsequent loss of a proton as illustrated below. Since the amount of ether



43 19

19 decreases at a slow rate, this compound must be stable.

Most of the carotol (1), though, is dehydrated to daucene (9). The conformation with the least amount of steric interaction is one in which the seven membered ring

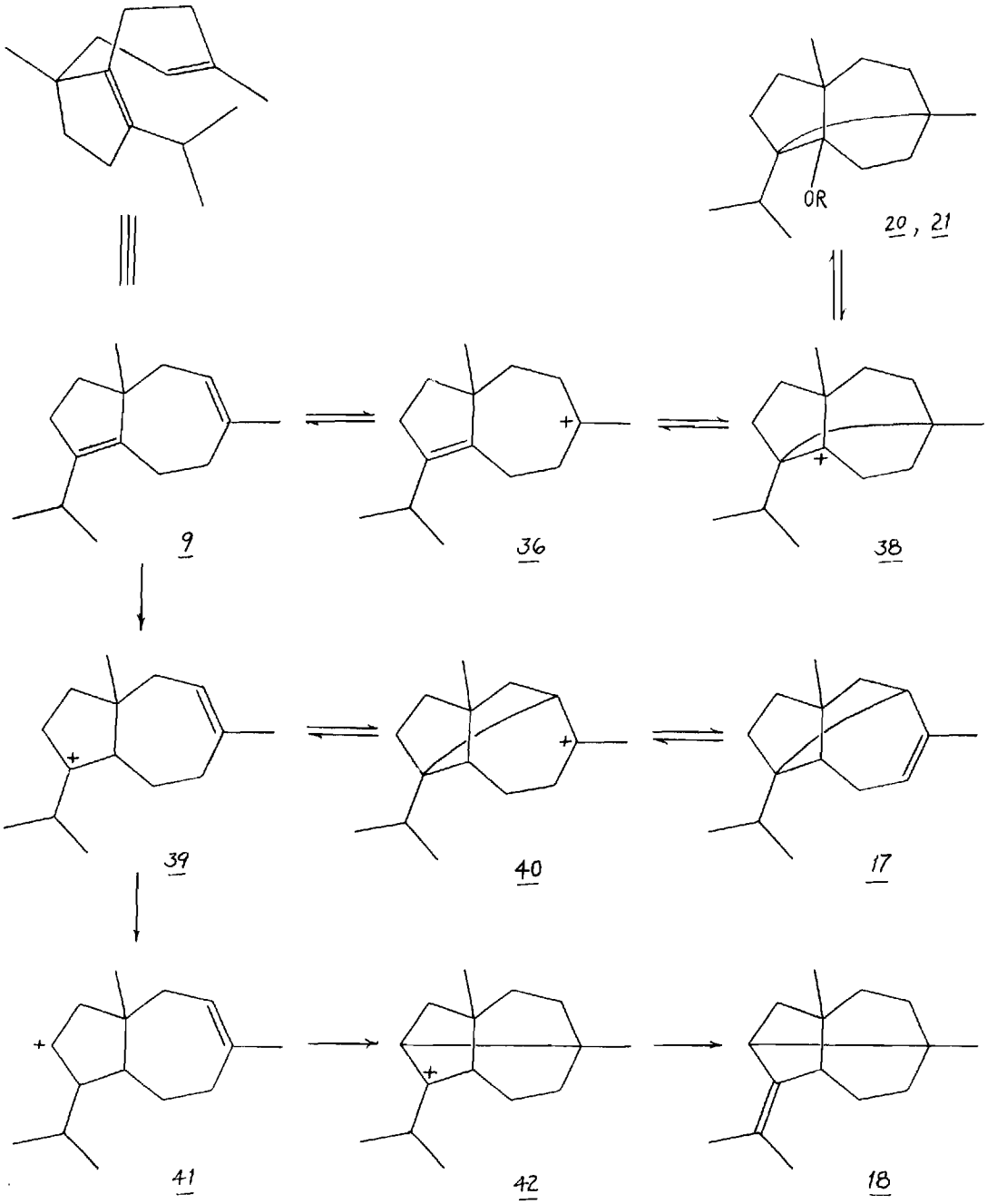


Figure 11. Mechanism of Interconversion of Formolysis Products

is in a "boat-like" conformation placing the double bonds in proximity of each other. Protonation to ion 36 would then result in immediate reaction with the remaining double bond to produce 38, followed by capture of a formate ion to give the kinetically favored tricyclocarotol ester (21) which yields the alcohol 20 on hydrolysis. However, the steric compression between the methyl and isopropyl would be the driving force for the reversal of the sequence.

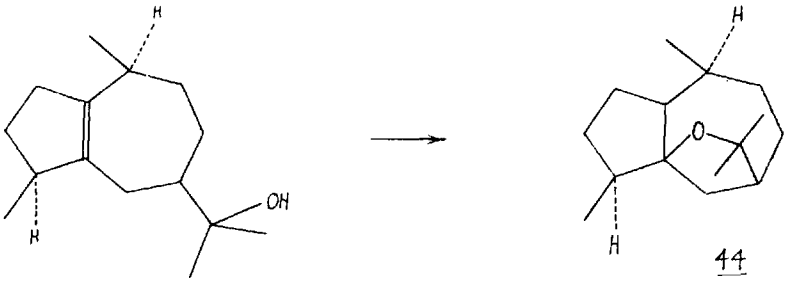
Protonation of daucene (9) in the five membered ring followed by reaction of the double bond with the proximal ion in 39 would give 40 and loss of a proton would yield tricyclodaucene (17). In this product there is no interaction of any of the atoms as seen by the spatial drawing of 17 in Figure 2. However this product still rearranges to a thermodynamically more stable olefin 18 through carbonium ion 39, a hydride shift to give ion 41, bridging by interaction of the double bond and ion to form the tricyclic ion 42 and loss of a proton to yield isotricyclodaucene (18). As with tricyclodaucene (17), Figure 11, there is no interaction of the atoms of this molecule, however, the double bond is exocyclic making this skeleton 18 less strained than that of 17.

In this postulated mechanism some of the cations formed such as 38 and 41 are less table then the ones they are produced from. Dauben, in his discussion of the acid rearrangement of the sesquiterpene thujopsene to a bicyclic

diene then to a tricyclic olefin, also finds this to be true.[18b] His explanation that the driving force for the reaction is the low free energy content of the final product, while the intermediates function to provide a route would be applicable here. Also as in Dauben's discussion energy would be attained from the net transformation of a carbon-carbon double bond to a carbon-carbon single bond.

Daucane ether (19) was assigned its structure in agreement with Clower for the following reasons.[24] The IR spectrum did not show any absorptions for functional groups except for C-O at 1110 and 1040 cm^{-1}. Also, the mass spectrum with a molecular ion at m/e 222 and base peak m/e 179 (M^+-C_3H_7) along with the elemental analysis conformed to the given structure. Unlike the other products its ORD curve was plane negative, while the ^{1}H-NMR had an upfield methyl singlet (δ0.73), two doublets (δ0.85, 1.13) for isopropyl methyls along with a singlet (δ1.22) for the methyl on the carbon with the ether linkage; and the ^{13}C-NMR, in its off resonance decoupled spectrum, had two singlets (δ92.8, 77.3) for ether carbons and one (δ44.0) for the quaternary carbon. Since the ether 19 is made in the beginning stages of formolysis and as seen from the results of the time study converts to the other tricyclic products, it is assumed that the five-seven membered ring is intact and the structural assignment is as presented. This type of ethereal product 44 is also seen during the formolysis of guaiol 43

as illustrated below.[51]



An attempt was made to synthesize the ether from daucol (3) as seen in Figure 12, preparing daucol (3) as

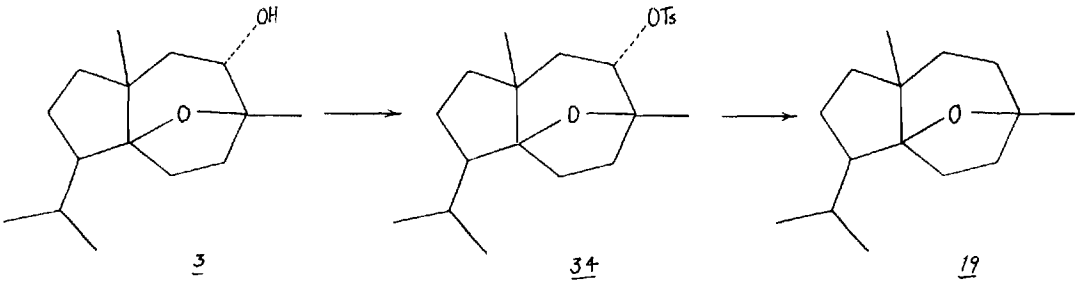
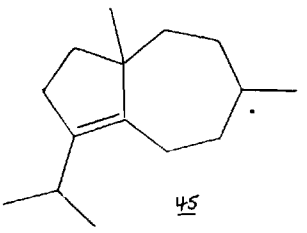


Figure 12. Attempted Synthesis of Daucane Ether

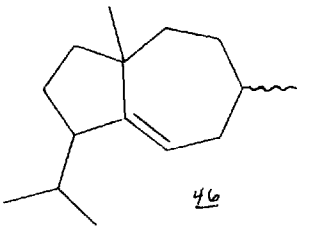
described in the literature.[14] The tosylate 34 was prepared and had characteristic absorptions in the IR as well as an ^{1}H-NMR in agreement with the structure. It was obtained as an oil with a carbon and hydrogen analysis in agreement with its structure and therefore used as such for subsequent experiments.

Since a first attempt to reduce the tosylate 34 with lithium aluminum hydride resulted in the recovery of daucol (3), a reagent, lithium triethylborohydride, that is reported to specifically avoid this side product was used.[43] However unreacted daucol tosylate (34) was recovered from the reaction.

In comparing the mass spectra of these compounds, it was found that the fragmentations were characteristic for the bicyclo and tricycloskeletons. With the bicyclocompounds carotol (1) and daucene (9) including the olefins 45, 46 below that Clower studied,[24] the base peak was that for loss of an isopropyl. The next highest fragments for carotol (1)



45



46

were m/e 123 (27%) and m/e 119 (35%), while that for daucene (9) was m/e 121 (45%). In compound 53 with the double bond in the five membered ring loss of a methyl also gave the fragment m/e 191 (42%, M^+-CH_3), the next group of significantly high fragments for all four compounds was at m/e 107 or 105 followed by at least one of the following fragments m/e 95, 93 or 91. The saturated carotane (daucane) (2), itself, also fit this pattern with the following fragments m/e 193 (54%, M^+-CH_3), 165 (85%, $M^+-CH_3H_7$), 123 (95%), 124

(68%), 109 (94%), 95 (100%), 96 (60%), 97 (43%).

With the major tricyclic compounds as seen by the spectra in Plates III, VI, IX, and XII, loss of an isopropyl results in a major fragment too. It is the base peak for tricyclocarotol (20) m/e 179 and daucane ether (19) m/e 179, while it is a smaller ion for the olefins 17 m/e 161 (26%) and 18 m/e 165 (48%) which also loses a methyl from the molecular ion to give m/e 189 (26%, M^+-CH_3). The next characteristic fragment in the tricyclic compounds is not common for the bicyclic ones that is one or more of the following m/e 139, 137, 136 or 133 as follows: 20 m/e 139 (40%), 137 (36%), 136 (24%); 17 136 (26%); 18 136 (27%), 133 (34%); and 19 139 (85%). The ether 19 does not have any of the smaller typical fragments, while the rest of the mass spectra for 17, 18 and 20 are very much like those of the bicyclic compounds as seen below: 17 m/e 123 (100%), 105 (36%); 18 m/e 120 (25%), 121 (31%), 119 (50%); 20 m/e 123 (27%), 121 (24%), 109 (30%), 107 (22%), 105 (28%), 95 (30%).

In another study, an attempt was made to effect a biosimulated synthesis of the daucane (2) skeleton. Nerolidol (47) was converted into the cycloheptenone 49 as seen in Figure 13, by heating the initially formed bromo preursor 48 in the base collidine at a sufficiently high temperature (160-170°C) to accomplish the [3,3] sigmatropic rearrangement to result in the desired product 49 using a method described

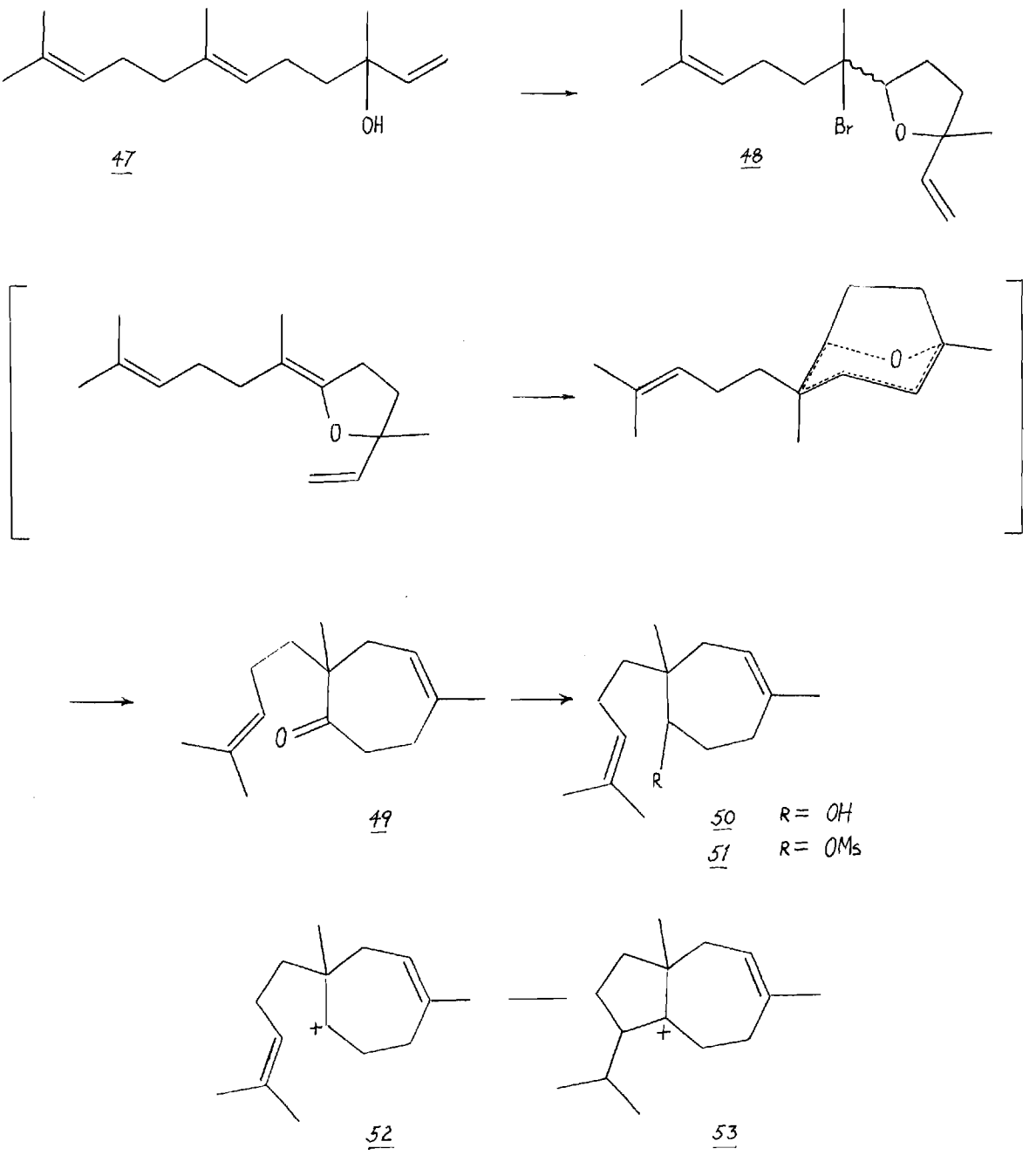


Figure 13. Biogenetic Type Synthesis of Carotane Skeleton

by Demole.[54] The spectral properties of the product obtained agreed with those reported. Ultimately, the goal was to obtain a positive charge in the ring as in ion 52. This intermediate is similar to that postulated in the biogenesis of carotol (1) as seen in Figure 1.[16] By reducing the ketone with hydride and varying the nature of the leaving group and the conditions, the five-membered ring should cyclize to give ion 53 and ultimately daucane products 2.

The alcohol 50 was obtained with spectral properties as described previously.[24] When it was heated with tosyl chloride in pyridine, the resultant product had properties consistent with an olefin formed from the addition of tosylate with subsequent elimination. The mesylate 51 was prepared and used without purification.

First the alcohol 50 was reacted for 20 minutes. The major products were the alcohol 50 and its formate. This was proved by hydrolyzing the formate and recovering starting alcohol 50. When the reaction was done for a longer time, a large mixture of products was detected by glc. Formolysis of the ketone 49 produced an ester whose reduction product had different spectral properties than above. There was no evidence of formation of a daucane product 2. Using acetic acid and formic acid in separate experiments with the mesylate 51 the major products were found to be olefinic by glc. An attempt was made to separate the olefins by silica gel chromatography. However, they were eluted together. The

^{1}H-NMR of the mixture showed all methyl signals downfield (1.50-1.77) as a complex multiplet. This would mean that the methyl had migrated with loss of a proton to place all of the methyls on double bonds. At this point work was discontinued on this project.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Acid catalyzed rearrangements of the sesquiterpene carotol (1) in formic acid have been studied. During the initial stages daucene (9) and the acoradienes (16) were formed; then they were converted to five new products: tricyclodaucene (17), isotricyclodaucene (18), daucane ether (19), tricyclocarotol (20) and tricyclocarotol formate (21). The structures of 20 and 17 were determined by spectral methods and verified by x-ray analysis of the p-iodobenzoate 22 and diol 23 respectively; while that of 19 was deduced from spectral evidence and that of 18 was determined by spectral evidence of it along with several reaction products. Perhaps a derivative of one of the reaction products of 18 could eventually be obtained in a crystalline form for x-ray analysis to conclusively prove its structure.

Also the results from the ORD experiments show that tricyclocarotol (20) isolated after two days of formolysis at 25°C has lower values than that from five days of formolysis at 25°C. It would be interesting to isolate tricyclocarotol (20) periodically from one day to five days to see if the speculation that the acoradienes (16) present in the beginning

are the contributing factor to the lowered values in the ORD curve. Another set of experiments could also be done at 45°C to see how the increased temperature would affect racemization. In order to show that daucene (9) is not racemized, it could be subjected to formolysis and recovered obtaining an ORD curve in both cases to see if they have the same values.

To increase the understanding of the mechanism an attempt could be made to isolate the unidentified products. Perhaps some of them would be related to the intermediates in Figure 11. An investigation of different acidic media would also be important. For instance a homogeneous system such as perchloric acid and dioxane that carotol (1) and its products are soluble in would show whether the ratio of products obtained change because of solubilities rather than stability. Varying the strength of acids might also change rates, product ratios and perhaps produce new products. The recent advent of carbonium ion stabilizing solvents has also opened up new possibilities for terpene rearrangements.[51]

It was shown in one experiment that the acoradienes (16) produced the same reaction mixture as carotol (1) during formolysis. Additional studies could be done on the interconversion of these skeletons. Conditions might also be found that would increase the yield of these spiro compounds and thus alter the course of the reaction.

Another attempt should be made in the biosimulated

synthesis of carotane sesquiterpenes from the cycloheptane skeleton 49, choosing additional leaving groups and acidic media to effect the ring closure.

In view of biogenetic postulations concerning the relationships of isoprenoid skeletons, the ultimate goal would be to isolate one or more of these new compounds from the oil of a plant, such as Daucus carota (Linn.), which contains carotol (1). This would verify the fact that these rearrangements actually do occur in vivo.

APPENDIX

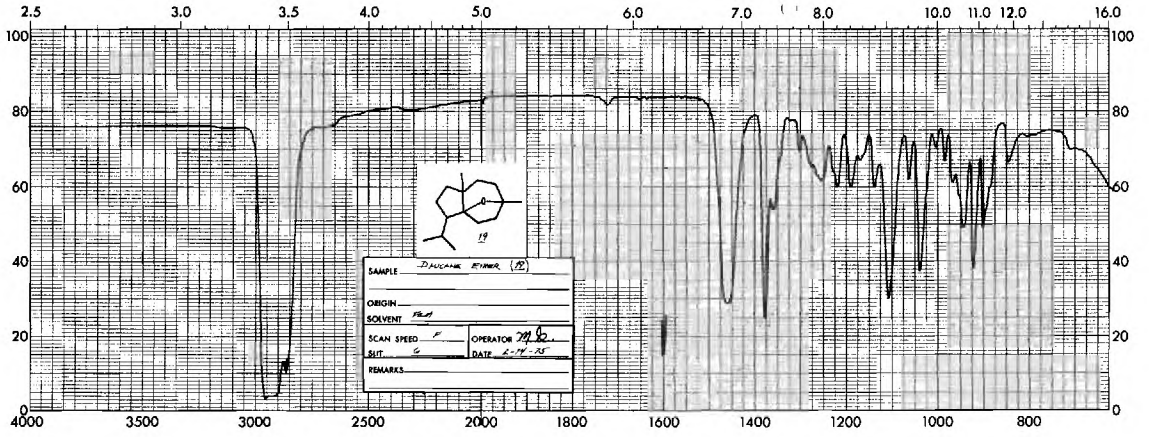


Plate I. Infrared Spectrum of Daucane Ether (19).

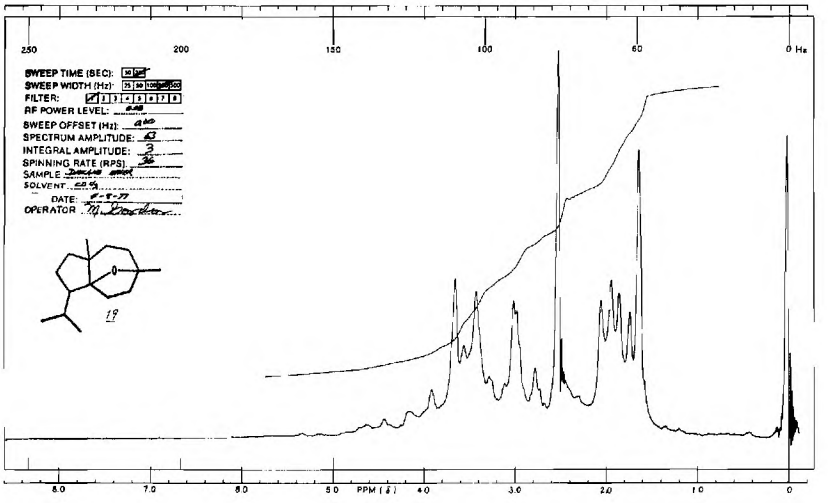


Plate II. ^{1}H-NMR Spectrum of Daucane Ether (19).

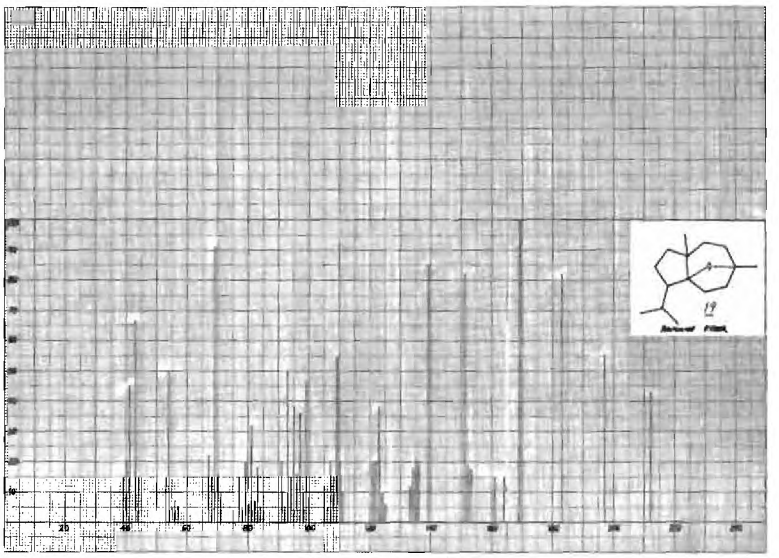


Plate III. Mass Spectrum of Daucane Ether (19).

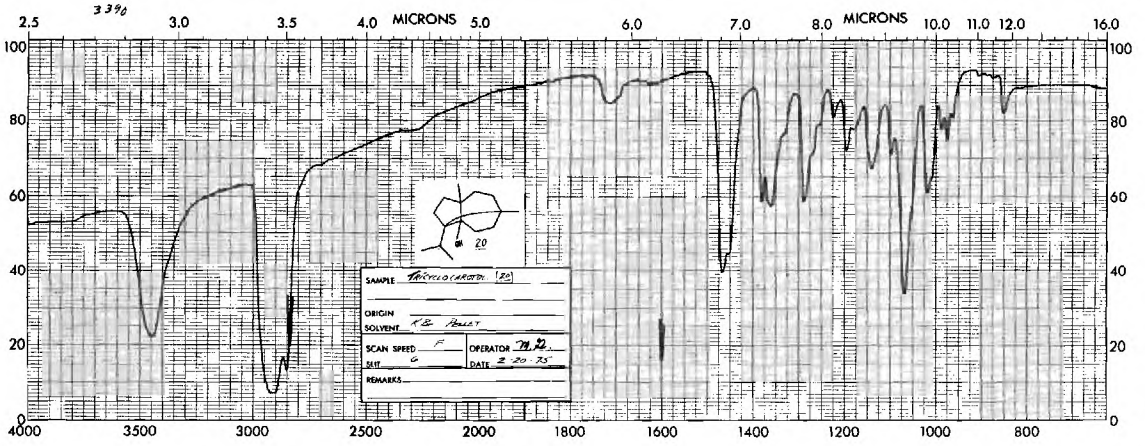


Plate IV. Infrared Spectrum of Tricyclocarotol (20).

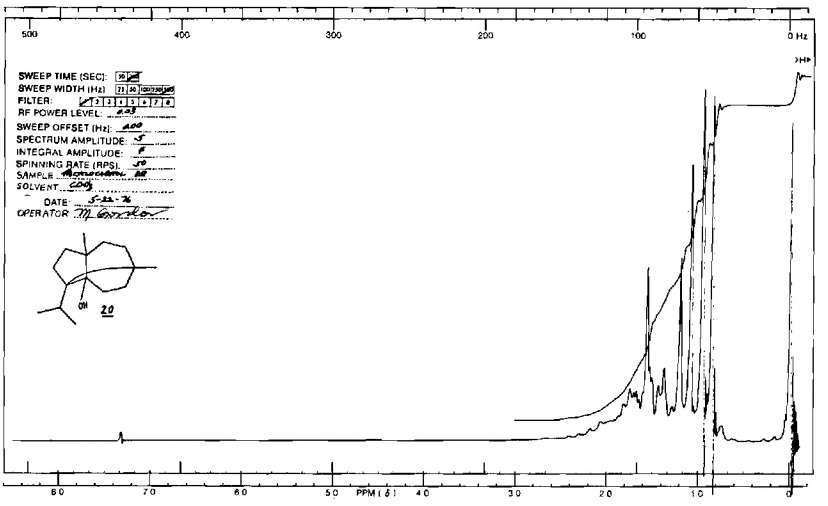


Plate V. ^{1}H-NMR Spectrum of Tricyclocarotol (20).

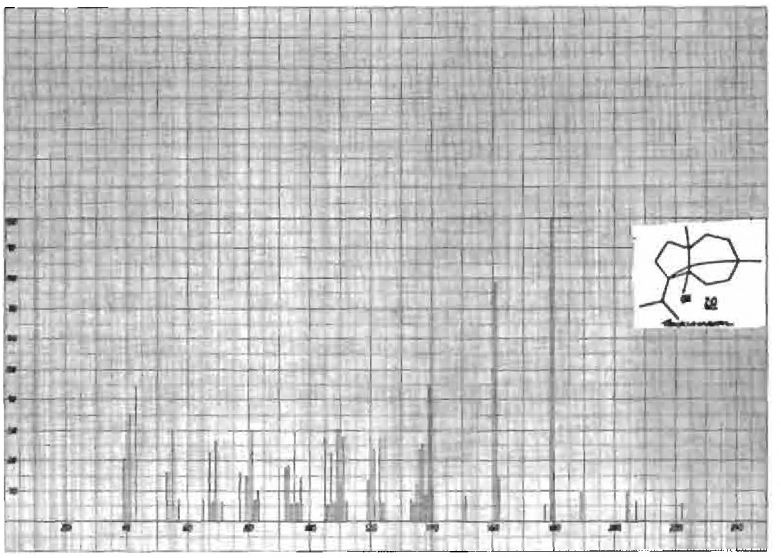


Plate VI. Mass Spectrum of Tricyclocarotol (20).

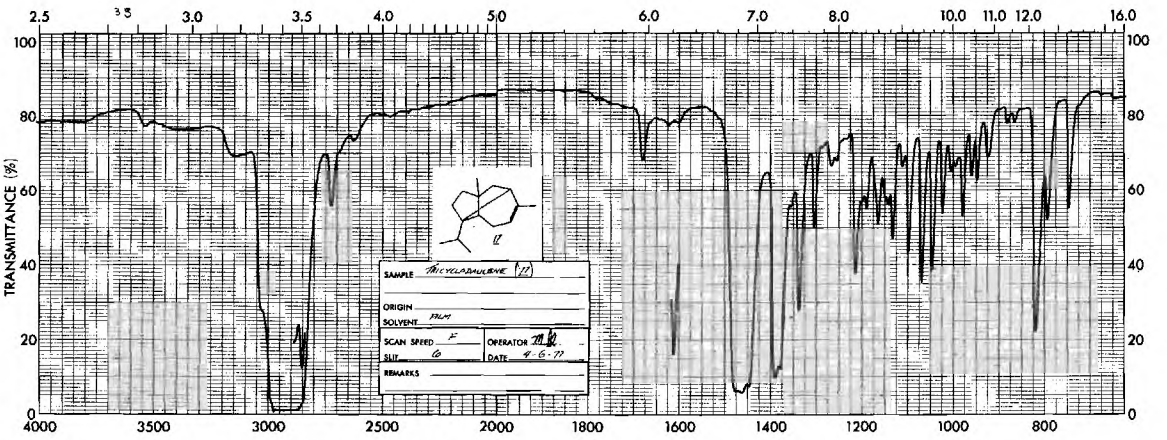


Plate VII. Infrared Spectrum of Tricyclodaucene (17).

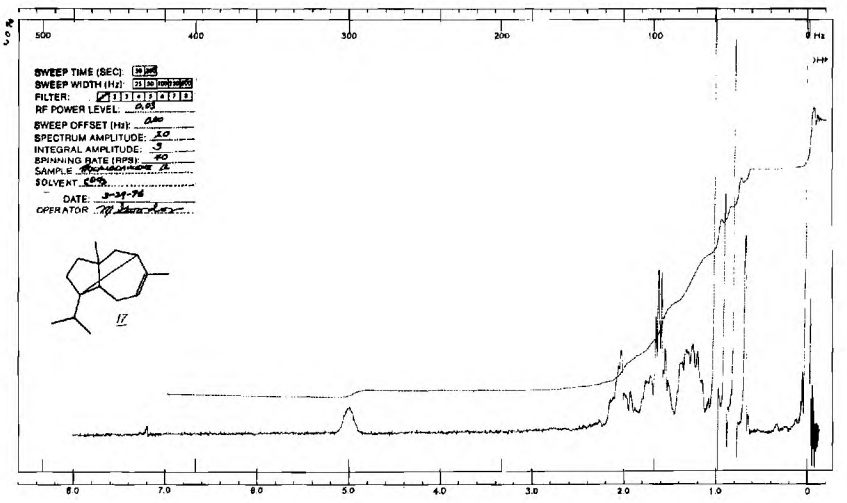


Plate VIII. ^{1}H-NMR Spectrum of Tricyclodaucene (17).

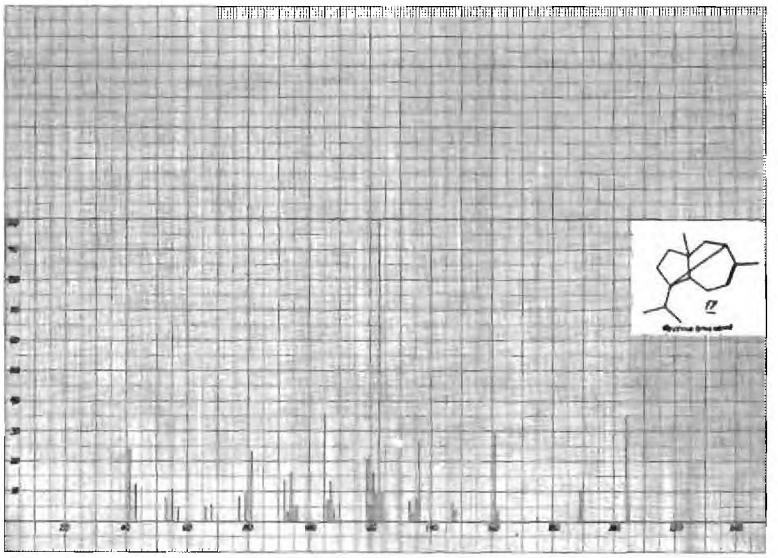


Plate IX. Mass Spectrum of Tricyclodaucene (17).

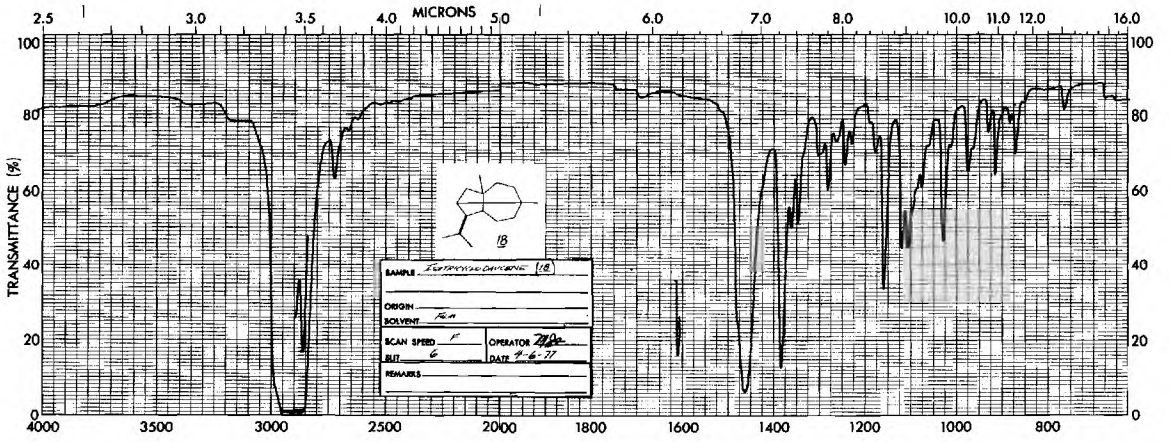


Plate X. Infrared Spectrum of Isotricyclodaucene (18).

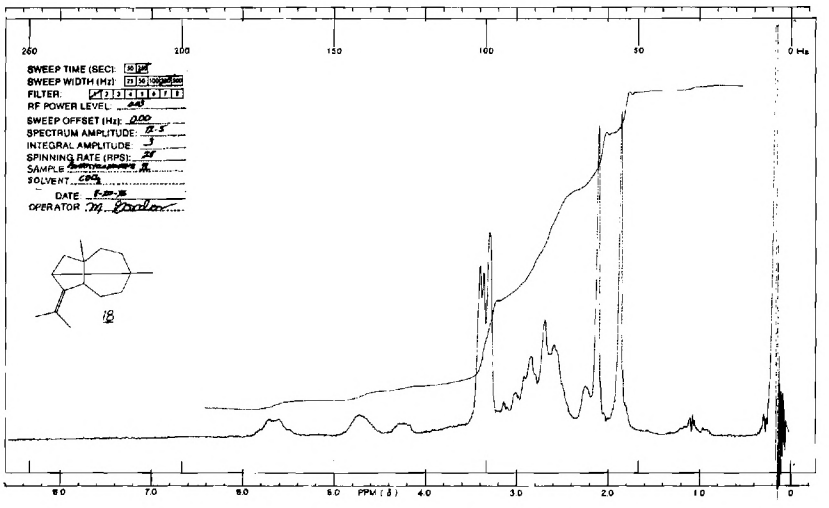


Plate XI. ^{1}H-NMR Spectrum of Isotricyclodaucene (18).

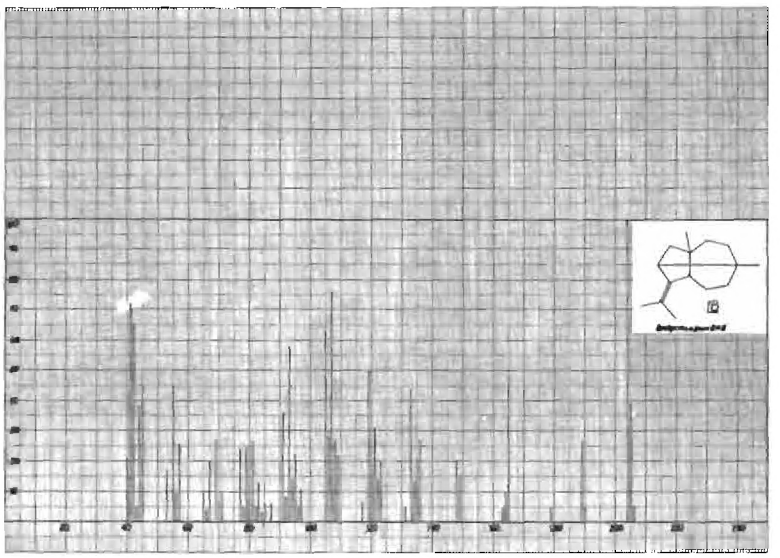


Plate XII. Mass Spectrum of Isotricyclodaucene (18).

Table 19. Tricyclocarotol p-Iodobenzoate (22) Structure Factors

K	L	FO	FC
	H=-14		
0	2	13	14
0	4	9	8
0	6	12	11
0	8	5	6
0	10	12	11
1	0	12	12
1	2	13	13
1	3	13	13
1	4	11	10
1	5	5	4
1	6	16	16
1	7	7	7
1	8	8	7
1	9	6	3
1	12	11	10
2	1	23	23
2	5	23	22
2	7	5	3
2	9	14	14
3	0	6	6
3	1	9	9
3	2	6	8
3	3	13	12
3	4	8	9
3	5	13	13
3	7	9	7
3	8	7	6
3	9	6	6
4	1	5	5
4	2	12	13
4	3	8	7
4	4	6	3
4	5	8	7
4	6	11	11
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2	3	28	28
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2	12	4	3
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3	11	16	15

K	L	FO	FC
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4	2	10	11
4	4	29	29
4	5	12	12
4	6	11	10
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6	0	10	11
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6	3	11	11
6	4	5	4
6	5	14	14
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6	7	10	9
6	8	4	5
6	9	8	7
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7	5	11	10
7	6	4	4
7	8	9	11
7	9	6	6
7	10	6	8
8	0	7	6
8	1	5	0
8	3	7	7
8	4	9	6
8	7	5	3
8	8	13	13
8	9	8	11
9	2	7	5
9	8	9	8
9	10	8	7
10	5	4	1

H=-10

K	L	FO	FC
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0	6	12	12
0	8	58	60
0	10	24	24
0	12	26	25
0	14	12	10
1	0	30	29
1	1	43	44
1	2	28	28
1	3	15	15
1	5	16	18
1	6	19	18
1	7	22	21
1	8	32	31
1	9	10	12
1	10	27	28
1	11	6	4
1	12	9	9
1	14	10	10
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2	4	13	11
2	5	28	30
2	6	9	11
2	7	9	10
2	8	15	14
2	9	10	12
2	10	20	21
2	12	8	6
2	13	5	3
2	14	4	6
2	15	7	8
3	0	11	11
3	1	31	31
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3	3	21	21
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4	9	14	17
4	10	7	6
4	12	10	9
4	14	5	2
5	0	9	8
5	1	14	15
5	2	25	24
5	3	10	7

K	L	FO	FC
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5	6	8	8
5	7	11	11
5	8	15	16
5	9	10	11
5	10	11	10
5	11	13	13
5	14	6	7
6	1	8	9
6	2	7	7
6	3	22	22
6	5	11	10
6	6	6	5
6	7	10	10
6	8	18	16
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6	11	4	2
6	12	10	9
6	13	7	5
6	14	5	4
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7	4	4	2
7	6	7	7
7	7	22	21
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8	0	14	14
8	1	11	13
8	4	13	13
8	5	11	12
8	6	5	6
8	7	11	11
8	9	6	5
8	12	4	3
9	2	8	8
9	5	5	6
9	11	5	2
10	2	6	3
10	3	7	7
10	7	7	6
10	8	5	5
10	9	7	7
11	7	6	6

H= -9

K	L	FO	FC
0	2	46	45
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0	6	28	29
0	8	15	13
0	10	5	10
0	12	4	1
0	14	5	10
0	16	4	2

K	L	FO	FC
1	0	19	19
1	1	38	39
1	2	61	61
1	3	8	11
1	5	26	26
1	6	40	39
1	7	32	32
1	8	46	49
1	9	20	22
1	11	11	11
1	12	8	9
1	13	10	12
1	15	5	-2
1	16	5	0
2	0	35	34
2	1	12	13
2	2	5	7
2	3	50	50
2	4	10	8
2	5	16	16
2	7	56	58
2	8	17	18
2	9	16	16
2	11	18	20
2	12	6	7
2	13	21	19
2	14	4	6
3	0	31	30
3	1	36	34
3	2	16	18
3	3	3	3
3	4	20	20
3	5	41	39
3	6	27	28
3	7	53	52
3	8	15	17
3	9	17	16
3	10	19	20
3	11	27	27
3	13	7	7
3	14	7	8
3	15	10	8
4	0	42	42
4	2	29	29
4	3	9	8
4	4	34	35
4	5	15	15
4	6	12	12
4	7	23	22
4	8	21	21
4	9	21	22
4	10	9	11
4	11	8	7
4	12	10	9
4	13	14	14
5	0	8	7

K	L	FO	FC
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5	2	29	29
5	3	4	4
5	4	4	1
5	5	15	16
5	6	20	19
5	8	39	39
5	9	12	12
5	10	4	1
5	11	5	7
5	14	6	4
6	0	16	17
6	1	7	8
6	2	5	3
6	3	28	27
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6	7	17	18
6	11	5	7
6	14	7	6
7	0	9	9
7	1	15	15
7	2	5	5
7	3	8	9
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7	6	7	5
7	7	17	16
7	8	12	12
7	10	9	8
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8	7	5	6
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8	10	4	1
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9	8	6	6
9	9	6	6
10	6	8	8
10	10	5	3
11	4	5	4
11	8	7	6
12	3	6	3
12	4	5	3

H= -8

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0	6	15	14
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0	12	31	31
0	16	5	4
1	0	46	46
1	1	58	59
1	2	27	27
1	4	29	27
1	5	34	34
1	6	69	69
1	7	4	5
1	8	9	9
1	9	27	28
1	10	37	38
1	11	6	4
1	13	14	16
1	14	7	5
2	1	3	3
2	2	6	4
2	3	61	63
2	5	4	1
2	7	48	50
2	8	20	19
2	9	9	7
2	11	13	13
2	12	15	15
2	13	9	6
2	15	8	8
2	16	4	0
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3	6	18	18
3	7	5	3
3	8	3	6
3	9	14	13
3	10	12	11
3	13	14	13
4	0	29	29
4	1	25	27
4	2	43	41
4	3	3	2
4	4	44	43
4	5	22	22
4	6	21	21
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4	14	4	2
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5	12	7	6
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6	2	10	11
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10	7	9	9
11	0	5	4
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11	6	7	8
11	7	4	3
12	7	6	7

H= -7

K	L	FO	FC
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0	10	23	24
0	12	31	30
0	14	10	12
0	16	15	13
1	0	60	58
1	1	58	61
1	2	32	33
1	3	16	14
1	4	57	57
1	5	72	76
1	6	18	19
1	7	9	10
1	8	26	26
1	9	26	28
1	10	14	14
1	12	11	12
1	14	16	15
2	0	10	9
2	1	27	25
2	2	11	9
2	3	137	135
2	5	17	16
2	7	52	51
2	8	17	15
2	9	4	1
2	10	6	9
2	11	26	26
2	12	8	8
2	13	5	8
2	14	6	3
2	15	6	4
3	0	49	48
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3	4	22	25
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3	7	18	18
3	8	25	26
3	9	25	24
3	12	13	15
3	15	8	4
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4	2	22	22
4	3	32	30
4	4	35	37
4	5	12	13
4	6	38	40
4	8	18	17

K	L	FO	FC
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4	12	12	10
4	14	4	7
5	0	35	35
5	1	15	16
5	2	28	28
5	3	8	8
5	4	17	14
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6	5	13	13
6	6	7	9
6	7	16	16
6	8	5	4
6	11	16	16
6	13	6	5
7	0	23	20
7	1	14	14
7	2	4	4
7	3	8	7
7	4	21	20
7	5	33	34
7	6	29	29
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7	8	16	16
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9	9	6	5
9	10	5	3
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K	L	FO	FC
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10	3	5	3
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10	7	10	8
10	8	7	6
10	11	6	1
11	6	5	4
11	8	6	5
12	2	5	6
12	7	6	5
13	4	6	1

H= -6

K	L	FO	FC
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0	10	44	45
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1	2	65	64
1	3	28	26
1	4	114	111
1	5	39	41
1	6	30	31
1	7	14	14
1	8	54	55
1	9	16	17
1	10	13	11
1	12	4	5
1	13	21	21
1	14	5	1
2	1	47	48
2	2	17	15
2	3	56	59
2	4	41	41
2	5	13	12
2	7	67	66
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2	10	6	4
2	11	45	45
2	12	14	14
2	13	6	6
2	15	16	15
3	0	60	59
3	1	4	5
3	2	25	22
3	3	34	31
3	4	43	41
3	5	44	42
3	7	24	22
3	8	22	24
3	9	31	29

K	L	FC	FC
3	10	18	17
3	11	9	7
3	12	11	12
3	13	31	30
3	14	12	9
4	0	5	6
4	1	4	1
4	2	102	101
4	4	9	6
4	5	17	18
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4	11	21	22
4	13	5	5
4	14	6	5
4	15	8	7
5	0	45	47
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K	L	FO	FC
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8	5	18	17
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H= -5

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1	3	63	64
1	4	27	26
1	5	42	45
1	6	11	11
1	7	30	33
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2	0	10	10
2	1	94	92
2	2	27	28
2	3	99	101
2	5	74	70
2	6	16	18
2	7	65	65
2	8	5	5

K	L	FO	FC
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2	10	12	10
2	11	10	7
2	12	7	8
2	13	5	3
2	14	9	10
2	15	9	7
3	0	26	27
3	1	132	128
3	2	28	27
3	3	112	107
3	4	44	46
3	5	77	74
3	6	33	33
3	7	28	25
3	8	31	34
3	9	47	46
3	10	6	5
3	11	5	4
3	12	10	12
3	13	10	7
3	15	5	3
3	16	5	2
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4	4	17	18
4	5	19	20
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4	7	23	23
4	9	5	8
4	10	25	26
4	12	10	7
4	13	6	5
4	14	6	6
5	0	42	41
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5	2	7	9
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5	4	49	47
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6	12	16	16
6	14	5	4
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7	5	5	6
7	6	14	14
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7	8	27	29
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7	12	11	9
7	13	8	7
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9	11	10	9
9	13	5	3
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10	9	8	6
10	11	5	4
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11	4	4	1
11	8	5	3
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H= -4

K	L	FO	FC
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0	6	110	112
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0	12	4	2
0	14	21	19
0	16	10	6
1	0	93	91
1	1	31	33
1	2	67	63
1	3	73	70
1	4	104	104
1	5	37	37
1	6	45	43
1	7	42	45
1	8	76	74
1	9	25	26
1	10	6	7
1	11	25	27
1	12	24	24
1	14	8	7
1	16	5	5
2	0	22	22
2	1	139	135
2	2	12	7
2	3	43	42
2	4	18	16
2	5	128	127
2	6	71	66
2	7	29	26
2	8	3	2
2	9	22	24
2	10	14	11
2	11	25	24
2	13	7	10
2	14	5	5
2	15	11	8
3	0	44	45
3	1	45	44
3	2	26	25
3	3	50	48
3	4	16	20
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3	6	17	17
3	7	15	14
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3	10	15	16
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3	12	10	10
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8	10	6	4
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K	L	FC	FC
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9	4	10	9
9	7	10	9
9	8	4	2
9	9	4	2
9	10	4	3
9	11	5	0
9	12	9	9
9	13	9	6
10	1	14	13
10	2	17	15
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11	9	5	3
12	1	5	2
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12	3	9	9
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0	12	17	18
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1	0	133	130
1	1	9	10
1	2	80	75
1	3	82	85
1	4	114	113
1	5	68	69
1	6	27	27
1	7	76	77
1	8	56	57
1	9	20	19
1	10	13	13
1	11	27	31
1	12	9	7
1	13	9	7
1	15	4	5
2	0	14	13
2	1	151	147
2	2	38	34
2	4	9	10

K	L	FC	FC
2	5	126	121
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2	7	65	62
2	8	3	0
2	9	46	45
2	11	33	32
2	12	4	4
2	13	19	20
2	15	7	5
3	0	42	43
3	2	28	23
3	3	90	84
3	4	107	105
3	5	48	47
3	6	60	61
3	7	68	67
3	8	37	40
3	9	33	33
3	10	19	22
3	11	36	36
3	13	18	17
3	14	5	4
4	0	77	76
4	1	13	12
4	2	66	65
4	3	26	23
4	4	63	60
4	5	48	45
4	6	38	40
4	7	42	42
4	8	20	20
4	9	8	9
4	10	39	39
4	11	22	23
4	12	11	13
4	14	11	10
4	15	5	4
5	0	55	55
5	1	38	39
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5	7	22	24
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5	9	10	10
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5	11	7	9
6	0	26	26
6	1	51	53
6	2	10	12
6	3	18	17
6	4	7	7
6	5	43	42
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K	L	FC	FC
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6	8	14	15
6	9	22	24
6	10	11	11
6	11	11	9
6	12	10	11
6	13	7	6
6	14	4	4
7	0	4	1
7	2	11	7
7	3	32	33
7	4	25	23
7	5	14	15
7	6	15	14
7	7	16	15
7	9	17	15
7	10	6	7
7	11	12	12
7	12	5	3
7	13	7	7
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8	11	8	7
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9	1	16	17
9	2	10	15
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9	8	6	6
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9	12	4	3
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11	8	5	1
11	10	6	5
12	6	5	6
13	1	5	6
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K	L	FO	FC
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0	14	20	19
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1	1	27	20
1	2	188	182
1	3	111	109
1	4	35	35
1	5	37	35
1	6	20	20
1	7	43	46
1	8	37	40
1	9	5	5
1	10	22	23
1	11	9	10
1	12	11	10
1	13	10	8
1	14	4	3
1	15	7	7
2	0	3	2
2	2	60	60
2	3	28	21
2	4	39	35
2	5	75	74
2	9	55	58
2	10	5	5
2	11	10	13
2	12	11	12
2	13	28	28
2	14	4	5
3	0	57	53
3	1	94	89
3	2	102	101
3	3	86	83
3	4	27	29
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3	7	56	55
3	8	21	23
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3	13	10	9
3	14	4	1
3	15	8	7
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4	1	13	13
4	2	77	77
4	4	66	62
4	5	21	20
4	6	66	65
4	7	5	3

K	L	FO	FC
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4	11	12	13
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4	14	12	9
5	0	68	69
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5	9	6	7
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5	12	13	12
5	13	5	3
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7	0	13	11
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8	12	8	8
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9	12	5	1
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12	0	6	6
12	7	4	5
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H= -1

K	L	FC	FC
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0	12	42	44
0	14	12	9
1	0	32	30
1	1	81	76
1	2	42	42
1	3	101	106
1	4	59	60
1	5	9	10
1	6	84	85
1	7	66	71
1	8	45	48
1	9	17	19
1	10	63	65
1	11	8	8
1	12	22	20
1	14	12	11
1	15	9	8
2	0	35	37
2	2	10	8
2	3	63	58
2	4	2	5
2	5	110	111
2	7	21	21
2	8	18	17
2	9	67	70
2	10	4	4
2	12	12	12
2	13	15	15
3	0	39	40
3	1	199	187
3	2	62	62
3	3	106	102
3	4	31	34
3	5	31	28
3	6	42	44
3	7	71	70
3	8	11	11
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3	15	9	7
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4	1	81	77
4	2	37	40
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4	4	68	69
4	5	34	33
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7	10	8	7
7	11	5	3
8	0	49	49
8	1	33	38
8	2	13	13
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8	4	45	44
8	6	9	7
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8	9	11	11
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8	11	6	6
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9	1	12	17
9	2	19	21
9	3	9	13
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9	11	6	6
9	12	7	6
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10	4	6	10
10	6	10	11
10	7	6	7
10	8	7	4
10	11	5	5
11	0	5	8
11	4	10	10
11	7	4	4
12	0	7	6
12	2	7	8
12	5	6	5
12	6	5	5
13	2	7	7
13	3	4	0
14	0	5	7

H= 0

K	L	FO	FC
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0	4	193	194

K	L	FC	FC
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0	10	25	24
0	12	18	18
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1	2	171	168
1	3	47	51
1	4	67	72
1	5	44	44
1	6	116	120
1	7	45	48
1	8	6	5
1	9	22	23
1	10	9	10
1	11	36	37
1	12	15	14
1	13	6	6
1	14	5	3
1	15	13	11
2	0	148	137
2	1	39	45
2	2	31	31
2	3	113	109
2	4	26	24
2	5	70	72
2	6	4	3
2	7	39	43
2	8	4	6
2	9	53	56
2	10	13	13
2	11	12	13
2	13	20	19
3	1	130	128
3	2	29	30
3	3	91	91
3	4	23	24
3	5	25	24
3	6	54	55
3	7	48	50
3	9	23	23
3	10	16	18
3	11	46	47
3	12	11	10
3	13	8	9
3	14	9	11
4	1	67	68
4	2	54	52
4	3	46	45
4	4	74	75
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4	13	8	6
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5	10	5	5
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9	6	21	21
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9	11	5	6
9	12	4	2
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10	6	14	14
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11	4	9	10
11	6	6	9
11	10	10	7
12	0	6	8
12	2	4	5
12	5	5	7
12	6	4	5
13	2	6	4
14	1	5	6

H= 1

K	L	FC	FC
0	2	43	50
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0	6	3	1
0	8	91	94
0	10	6	6
0	12	33	32
1	0	30	30
1	1	109	107
1	2	95	98
1	3	105	107
1	4	10	12
1	5	92	98
1	6	84	86
1	7	35	39
1	8	25	25
1	9	19	20
1	10	36	39
1	11	15	14
1	12	5	6
1	13	7	8
1	14	15	13
2	0	34	37
2	1	37	37
2	2	17	19
2	3	98	96
2	4	2	4
2	5	106	109
2	7	49	51
2	8	18	17
2	9	20	19
2	10	5	3
2	11	11	13
2	12	5	4
2	13	11	10
3	0	39	40
3	1	30	28
3	2	87	88
3	3	77	78
3	4	9	8
3	5	59	56
3	6	45	47
3	7	21	22
3	9	10	9
3	10	19	21
3	11	15	13
3	13	7	8
3	14	6	6
4	0	66	66
4	1	47	47
4	2	22	20
4	3	26	27
4	4	84	85
4	5	32	31
4	6	5	8
4	7	14	15
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4	9	15	15
4	10	5	2
4	12	14	14
4	14	7	3
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6	3	13	13
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7	11	7	6
8	0	50	49
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K	L	FO	FC
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8	5	17	19
8	8	7	5
8	9	6	5
9	0	4	7
9	1	9	6
9	2	16	16
9	3	6	2
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10	9	5	4
11	1	9	10
11	3	8	8
11	4	6	6
11	5	6	8
11	6	8	7
12	0	8	6
12	4	8	7
13	3	6	6
14	0	6	7

H= 2

K	L	FO	FC
0	0	10	9
0	2	135	133
0	4	122	121
0	6	25	25
0	8	72	75
0	10	6	5
0	12	35	34
1	0	89	88
1	1	125	128
1	2	133	134
1	3	57	63
1	4	64	63
1	5	94	93
1	6	30	32
1	7	16	16
1	8	6	3
1	9	32	33
1	10	33	34
1	11	7	6
1	13	8	9
1	14	12	11

K	L	FC	FC
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2	1	3	7
2	2	11	14
2	3	136	137
2	4	24	25
2	5	13	9
2	6	10	12
2	7	63	63
2	8	6	5
2	9	28	28
2	11	28	28
2	12	7	5
2	13	14	11
3	0	55	53
3	1	102	100
3	2	78	78
3	3	23	22
3	4	29	29
3	5	109	112
3	6	38	40
3	7	19	20
3	8	13	13
3	9	48	48
3	10	15	16
3	11	10	8
3	13	10	10
4	0	81	85
4	2	16	15
4	3	37	37
4	4	102	101
4	5	22	23
4	6	14	13
4	7	29	29
4	8	27	30
4	9	6	5
4	11	5	5
4	12	15	15
4	13	7	5
5	0	68	69
5	1	44	43
5	2	62	63
5	3	26	26
5	4	6	5
5	5	35	34
5	6	9	9
5	8	12	9
5	9	4	3
5	10	20	20
5	11	7	3
5	12	5	6
6	0	9	8
6	1	9	9
6	2	7	5
6	3	50	50
6	4	37	42
6	5	7	6

K	L	FO	FC
6	7	26	26
6	9	14	12
6	11	12	11
7	0	13	11
7	1	43	44
7	2	17	13
7	3	4	3
7	4	16	14
7	5	37	39
7	6	19	16
7	7	5	5
7	8	19	21
7	9	13	14
7	11	4	3
8	0	9	8
8	2	6	8
8	3	8	11
8	4	22	20
8	5	10	10
8	6	15	15
8	7	7	10
8	8	13	11
8	9	4	3
9	0	11	13
9	1	13	10
9	2	5	5
9	3	8	7
9	4	9	10
9	5	4	8
9	6	8	9
9	8	7	7
9	10	9	8
10	0	19	19
10	1	18	17
10	3	10	9
10	4	11	14
10	5	9	8
10	6	10	9
11	0	9	10
11	1	4	4
11	3	11	11
11	8	6	3
12	0	7	6
12	1	7	8
12	2	5	4
12	6	5	4
13	0	4	5
14	0	5	4
14	2	6	2

H= 3

K	L	FO	FC
0	0	149	151
0	2	124	120
0	4	150	154
0	6	70	68

K	L	FO	FC
0	8	64	63
0	10	22	21
0	12	14	12
1	0	129	130
1	1	56	55
1	2	114	116
1	3	33	33
1	4	139	138
1	5	50	54
1	6	47	48
1	7	6	3
1	8	34	34
1	9	24	25
1	10	18	16
1	11	10	9
1	13	11	10
2	0	13	13
2	1	18	20
2	2	20	18
2	3	98	97
2	4	11	10
2	5	24	25
2	6	26	28
2	7	66	69
2	8	4	0
2	9	14	13
2	11	34	33
2	13	4	1
3	0	41	43
3	1	96	97
3	2	32	34
3	3	66	67
3	4	31	32
3	5	50	51
3	6	28	29
3	7	26	27
3	8	12	14
3	9	23	23
3	10	12	13
3	11	9	10
3	13	9	9
4	0	75	76
4	1	5	3
4	2	51	49
4	3	21	23
4	4	48	49
4	6	36	38
4	7	4	5
4	8	29	28
4	9	5	5
4	10	13	14
4	12	15	14
4	13	5	2
5	0	54	55
5	1	35	33
5	2	28	29

K	L	FO	FC
5	3	4	3
5	4	64	65
5	5	37	38
5	6	26	26
5	8	29	29
5	9	7	7
5	10	12	11
5	11	4	4
5	12	10	8
6	0	25	26
6	1	3	1
6	2	26	29
6	3	43	42
6	4	11	14
6	5	15	14
6	6	22	25
6	7	33	35
6	8	5	5
6	9	8	5
6	11	11	12
7	0	4	1
7	1	32	36
7	2	14	12
7	3	20	20
7	4	9	13
7	5	19	19
7	7	8	7
7	9	10	10
7	10	6	5
7	11	6	4
8	0	4	5
8	1	4	1
8	2	10	7
8	4	9	9
8	5	4	2
8	6	9	8
8	7	5	5
8	8	11	12
9	0	18	19
9	1	4	8
9	2	10	9
9	3	8	9
9	4	7	8
9	5	12	10
9	6	10	9
9	10	5	2
10	0	12	12
10	2	6	7
10	5	5	4
10	6	5	3
10	7	7	7
11	0	6	8
11	1	6	6
11	2	6	4

K	L	FC	FC
	H=	4	
0	0	38	40
0	2	58	58
0	4	43	40
0	6	43	46
0	8	21	22
0	10	28	28
0	12	12	9
1	0	91	91
1	1	104	108
1	2	39	40
1	3	64	60
1	4	26	25
1	5	53	55
1	6	38	40
1	7	11	9
1	8	21	21
1	9	28	27
1	10	24	23
1	12	17	16
1	13	8	8
2	0	21	22
2	1	46	45
2	2	12	14
2	3	127	128
2	5	27	26
2	6	3	2
2	7	71	72
2	8	3	3
2	9	10	9
2	10	5	2
2	11	23	23
3	0	43	45
3	1	89	90
3	2	46	48
3	3	61	60
3	4	52	53
3	5	41	43
3	6	21	22
3	7	18	19
3	8	21	22
3	9	24	24
3	10	12	12
3	11	6	6
3	12	5	5
4	0	34	34
4	1	7	7
4	2	85	86
4	3	28	28
4	4	22	23
4	5	11	10
4	6	45	46
4	7	12	13
4	8	20	20
4	9	7	7

K	L	FC	FC
4	10	14	15
4	11	7	5
4	12	12	10
5	0	46	48
5	1	42	42
5	2	21	21
5	3	6	6
5	4	26	27
5	5	5	3
5	6	35	34
5	7	9	9
5	8	24	24
5	9	6	5
5	10	17	15
5	12	7	8
6	0	12	12
6	3	43	43
6	4	8	6
6	5	6	7
6	6	4	3
6	7	18	19
6	9	5	3
6	11	6	6
7	0	14	11
7	1	21	24
7	2	17	17
7	3	31	32
7	4	32	30
7	9	5	7
8	0	27	28
8	2	25	25
8	3	6	8
8	4	15	15
8	6	17	17
8	7	6	6
8	8	4	1
8	10	5	5
9	0	5	8
9	1	4	3
9	2	14	15
9	3	12	13
9	4	13	16
9	5	7	3
9	8	7	6
10	1	5	3
10	2	5	3
10	3	11	10
10	5	6	6
11	0	5	3
11	1	10	10
11	4	6	4
13	1	6	5
13	3	6	5
13	4	8	7

K	L	FO	FC
	H=	5	
0	0	17	16
0	2	152	153
0	4	8	3
0	6	84	85
0	8	12	12
0	10	36	36
0	12	14	12
1	0	68	68
1	1	68	68
1	2	5	7
1	3	26	25
1	4	75	74
1	5	54	54
1	6	13	13
1	7	12	14
1	8	39	38
1	9	24	25
1	10	11	11
1	11	6	6
1	12	10	10
2	0	10	10
2	1	71	70
2	2	36	32
2	3	87	89
2	5	41	42
2	6	16	16
2	7	39	40
2	8	4	5
2	9	5	3
2	11	20	20
3	0	25	27
3	1	55	54
3	2	37	39
3	3	39	39
3	4	36	38
3	5	49	51
3	6	20	21
3	7	23	22
3	8	19	19
3	9	29	28
3	10	8	7
3	11	8	8
3	12	6	5
4	0	5	5
4	1	19	20
4	2	86	88
4	3	7	9
4	4	11	10
4	5	17	17
4	6	31	32
4	8	19	18
4	10	17	17
4	11	6	5
5	0	41	41

K	L	FO	FC
5	1	22	20
5	2	8	8
5	4	37	40
5	5	23	22
5	6	14	14
5	7	8	9
5	8	19	20
5	9	14	12
6	0	7	6
6	1	13	13
6	2	32	34
6	3	44	44
6	4	6	5
6	5	23	23
6	6	7	10
6	7	19	18
6	9	4	4
6	10	5	5
7	0	6	2
7	1	20	21
7	2	12	11
7	3	16	17
7	4	4	1
7	5	23	23
7	6	10	11
7	7	9	10
7	9	13	13
7	10	5	4
8	2	4	1
8	3	13	15
8	5	15	16
8	6	5	5
8	8	6	3
9	0	4	6
9	2	6	5
9	5	6	4
9	6	5	6
10	0	10	10
10	2	6	7
10	3	9	8
10	7	5	4
11	0	4	3
11	2	7	7
11	5	6	4
12	1	4	1
12	3	6	5

H= 6

K	L	FO	FC
0	0	16	15
0	2	111	111
0	4	9	8
0	6	60	58
0	8	15	15
0	10	26	26
1	0	102	104
1	1	58	59
1	2	6	5
1	3	45	48
1	4	77	77
1	5	31	34
1	7	28	27
1	8	29	28
1	9	14	16
1	11	7	6
2	1	82	84
2	2	20	21
2	3	43	44
2	4	9	6
2	5	29	30
2	6	5	6
2	7	39	38
2	9	21	22
2	11	19	17
3	0	57	59
3	1	37	37
3	2	11	12
3	3	36	35
3	4	46	47
3	5	39	38
3	6	8	9
3	7	29	30
3	8	11	12
3	9	17	17
3	11	6	4
4	0	4	6
4	1	14	13
4	2	61	62
4	3	7	7
4	4	11	13
4	5	12	12
4	6	29	29
4	7	4	3
4	8	6	6
4	9	5	8
4	10	20	20
5	0	43	47
5	1	31	32
5	2	6	5
5	3	25	25
5	4	45	47
5	5	18	16
5	6	9	10
5	7	6	5
5	8	13	13
5	9	8	8
6	1	36	36
6	2	6	9
6	3	15	15
6	4	9	9
6	5	5	7
6	7	15	14
6	10	6	4
7	0	13	12
7	1	9	12
7	4	10	7
7	5	16	15
7	7	7	8
7	8	7	4
7	9	9	9
8	0	5	5
8	1	8	11
8	2	27	26
8	4	12	13
8	6	11	10
9	0	13	14
9	1	20	20
9	2	4	3
9	3	13	11
9	4	10	11
9	6	5	3
10	0	5	7
10	1	9	8
10	2	6	9
10	3	4	2
12	4	5	1

H= 7

K	L	FO	FC
0	0	52	52
0	2	70	71
0	4	22	20
0	6	55	57
0	8	10	9
0	10	24	22
1	0	59	58
1	1	40	43
1	2	35	34
1	3	67	65
1	4	26	27
1	5	15	16
1	6	15	14
1	7	21	20
1	8	27	27
1	9	10	9
2	0	10	9
2	1	77	78
2	2	9	9
2	3	15	17
2	4	18	17
2	5	31	32
2	7	28	29
2	9	28	28
3	0	47	48
3	1	27	28
3	2	13	13
3	3	70	70
3	4	30	31
3	5	12	13
3	6	6	8
3	7	20	20
3	8	16	16
4	0	29	30
4	1	23	24
4	2	41	43
4	3	11	13
4	4	5	5
4	6	45	46
4	8	5	4
4	9	7	7
4	10	20	19
5	0	33	35
5	1	18	18
5	2	25	24
5	3	18	16
5	4	17	17
5	5	10	10
5	6	12	14
5	7	5	6
5	8	20	20
5	9	5	6
6	0	27	28
6	1	27	27
6	2	5	6
6	4	17	18
6	5	13	15
6	6	8	8
6	7	8	9
6	9	10	9
7	0	21	20
7	1	7	7
7	2	8	11
7	3	27	28
7	4	14	13
7	6	4	5
7	7	8	9
8	1	16	17
8	2	19	19
8	3	9	9
8	4	10	10
8	6	13	12
9	0	4	7
9	1	4	2
10	5	6	5
10	6	5	3
11	2	5	3
11	3	8	8
11	4	5	5

H= 8

K	L	FO	FC
0	0	41	40
0	2	75	76
0	4	13	12

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
0	6	43	42	8	3	13	14	7	0	9	9	7	1	16	17
0	8	22	21	8	4	7	7	7	1	8	7	7	2	12	13
1	0	46	46	8	5	7	8	7	4	9	8	7	3	13	14
1	1	5	5	9	2	15	14	8	0	7	6	7	4	9	9
1	2	41	41	10	0	9	9	8	2	5	8	7	5	7	7
1	3	42	43	10	1	4	4	8	3	5	5	8	0	13	14
1	4	38	37	10	3	7	7	9	0	5	8	8	4	6	6
1	6	20	18	11	0	5	4	9	3	7	7	9	1	11	12
1	7	20	21	11	1	5	3	9	4	9	9	10	1	6	5
1	8	20	19					10	1	8	6				
1	9	7	7		H=	9		10	3	7	6		H=	11	
2	1	78	80					11	1	8	5				
2	2	4	5	0	0	89	89					0	0	41	40
2	3	9	10	0	2	6	6		H=	10		0	2	12	12
2	5	62	62	0	4	44	43					0	4	36	36
2	7	9	8	0	6	23	23	0	0	44	46	1	0	17	17
2	8	4	4	0	8	20	20	0	2	20	20	1	1	11	13
2	9	24	23	1	0	18	19	0	4	42	41	1	2	30	29
3	0	41	43	1	1	8	7	0	6	12	12	1	3	17	18
3	2	34	36	1	2	56	55	1	0	30	29	1	5	9	9
3	3	46	48	1	3	21	21	1	1	33	33	1	6	18	17
3	4	18	18	1	4	28	29	1	2	17	19	2	1	23	23
3	6	6	4	1	6	26	26	1	3	33	32	2	3	22	22
3	7	26	25	1	7	18	18	1	4	10	9	2	5	17	17
3	8	12	11	1	8	11	11	1	5	9	10	2	6	5	2
3	9	5	3	2	0	34	34	1	6	19	18	3	1	12	11
4	0	28	29	2	1	52	52	1	7	16	15	3	2	16	16
4	1	22	24	2	2	20	20	2	0	5	4	3	3	20	19
4	2	44	45	2	3	21	21	2	1	36	38	3	4	6	6
4	3	24	24	2	4	14	13	2	2	5	4	3	5	11	11
4	4	4	5	2	5	43	43	2	3	17	17	4	0	28	29
4	5	16	17	3	0	30	30	2	5	33	33	4	2	12	10
4	6	28	29	3	2	15	14	2	7	15	13	4	3	14	14
4	8	10	9	3	3	10	10	3	0	11	11	4	4	23	24
4	9	6	3	3	4	18	18	3	1	53	54	5	0	13	15
5	0	33	34	3	6	6	6	3	2	17	18	5	1	12	13
5	1	16	16	3	7	16	16	3	3	32	32	5	2	15	17
5	2	30	32	3	8	8	8	3	4	7	8	5	3	11	11
5	3	9	9	4	0	39	42	3	5	19	19	6	0	11	11
5	4	20	20	4	1	4	4	3	6	10	10	6	1	7	8
5	5	10	10	4	2	4	5	3	7	16	15	6	3	7	7
5	6	9	9	4	3	14	15	4	0	33	34	6	4	7	7
5	8	8	9	4	4	22	22	4	2	12	11	7	0	13	14
6	0	6	6	4	6	16	16	4	3	15	16	7	3	7	7
6	1	32	33	4	8	16	15	4	4	29	30	8	0	8	6
6	2	14	15	5	0	7	7	4	6	7	7	9	0	4	2
6	3	4	4	5	2	33	34	5	0	8	8	9	1	7	6
6	4	8	7	5	3	16	17	5	1	8	8				
6	5	22	21	5	4	16	16	5	2	10	11		H=	12	
6	7	6	6	5	6	17	17	5	3	10	11				
7	0	5	3	5	7	8	8	5	4	4	2	0	0	35	34
7	2	5	4	6	0	16	17	5	6	12	12	0	2	11	12
7	3	13	14	6	1	29	29	6	1	11	12	0	4	26	25
7	5	6	5	6	2	23	23	6	4	11	12	1	0	13	14
7	7	14	14	6	4	11	12	6	5	13	13	1	1	18	18
8	0	10	10	6	5	15	16	7	0	8	8	1	2	23	23

K	L	FO	FC	K	L	FC	FC	K	L	FO	FC	K	L	FO	FC
1	3	12	11												
1	4	11	11												
2	1	15	15												
2	2	11	10												
2	3	22	21												
3	1	16	16												
3	2	12	13												
3	3	11	9												
4	0	23	24												
4	4	15	15												
5	0	7	8												
5	2	13	11												
5	3	5	7												
6	1	9	8												
6	2	10	11												
7	1	6	6												
8	0	5	7												
	H=	13													
0	0	23	22												
1	0	16	15												
1	1	17	16												
1	2	14	14												
1	3	5	4												
2	3	23	22												
3	1	18	18												
3	2	10	11												
4	0	15	14												
4	1	9	9												
5	0	8	9												
5	1	5	3												
	H=	14													
0	0	9	9												
1	0	12	12												
1	1	10	10												
3	0	5	6												

Table 20. Diol 23 Structure Factors

K	L	FO	FC	K	L	FO	FC	K	L	FC	FC	K	L	FO	FC
	H= 0			7	6	13	13	1	5	13	13	6	8	5	3
				7	7	6	7	1	6	3	4	6	9	4	3
0	2	123	133	7	8	13	12	1	7	8	9	7	0	35	29
0	4	38	37	7	10	5	4	1	9	7	7	7	1	3	3
1	1	26	24	8	0	9	9	1	10	7	7	7	2	20	20
1	2	15	16	8	2	25	26	2	0	28	32	7	3	4	4
1	3	37	32	8	3	6	3	2	1	74	74	7	4	13	15
1	6	16	17	8	4	13	12	2	2	11	9	7	5	9	8
1	7	13	13	8	5	10	9	2	3	24	22	7	6	21	20
1	8	13	11	8	6	7	7	2	4	14	13	7	7	8	7
1	9	5	6	8	7	7	6	2	5	7	9	7	8	8	7
1	10	5	5	8	9	5	3	2	6	3	2	7	10	4	3
1	12	9	7	9	1	8	12	2	7	9	8	7	11	5	0
2	0	73	75	9	2	12	9	2	8	12	12	8	0	17	18
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0	0	16	13
0	2	8	8
0	3	11	16
0	5	8	10
1	2	7	10
1	5	4	5
2	0	16	17
2	1	10	11
2	2	10	11
2	3	6	7
2	4	6	9
2	8	5	5
3	2	6	8

K	L	FO	FC
3	4	6	8
3	7	4	4
4	1	7	6
4	5	5	6
5	1	13	14
5	3	11	11
5	5	6	5
6	0	6	4
6	3	4	1
6	5	5	2
7	0	9	10
7	2	6	7
8	2	7	7
8	4	6	5
10	0	5	3
	H=	9	
0	1	10	10
0	2	4	3
0	3	6	10
0	4	6	7
1	0	4	1
2	1	10	11
2	3	5	5
3	3	5	4
4	3	5	6
5	1	4	5
6	5	4	2
	H=	10	
1	3	5	3
2	2	4	0
3	0	4	4
4	0	5	6
5	1	4	4
5	3	5	4
5	5	5	1
6	0	6	7
	H=	11	
1	4	5	0

K	L	FO	FC

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VITA

Maureen Miller Gordon was born in Newark, New Jersey on October 2, 1941 to Nat and Elaine Miller and lived in Passaic, New Jersey with her parents and younger brother, Kenneth, until 1963. Upon graduating from Passaic High School in 1958, she attended Douglass College, Rutgers University in New Brunswick, New Jersey, receiving her AB in Chemistry in 1962.

For the next year she worked in the Natural Products Division of Schering Corporation, Bloomfield, New Jersey. She married Stephen Gordon on August 19, 1963 and moved to Baltimore, Maryland, where her husband was attending the University of Maryland Medical School. There she was employed by the Biochemistry Research Department of Sinai Hospital.

In July, 1967 the Gordons moved to Philadelphia, Pennsylvania, where Maureen was employed for two years in the Division of Molecular Biology of Childrens' Hospital. Maureen has lived in Atlanta, Georgia since 1970 when Stephen entered private practice in Obstetrics and Gynecology. They have three children, Penny, Heidi and Adam born in 1967, 1969 and 1971, respectively.

Maureen entered Georgia Institute of Technology in 1972 as a special student becoming a graduate student in 1973, graduating with a Ph.D. in Chemistry in 1977.

ERRATA

Page v, line 15: 163, read 163a.

Page 1, line 15: alanite, read alanate.

Page 38, line 12: quartenary, read quaternary.

Page 48, line 8: organge, read orange.

Page 51, line 9: cellite, read celite.

Page 52, line 6: analysis, read analyses.

Page 77, line 8: cellite, read celite.

Page 89, line 6: quartenary, read quaternary.

Page 105, line 8: in tact, read intact.

Page 105, line 9: quartenary, read quaternary.

Page 110, line 12: quartenary, read quaternary.

Page 113, line 12: quartenary, read quaternary.

Page 113, line 20: quartenary, read quaternary.

Page 113, line 24: this, read these.

Page 116, line 11: this, read these.

Page 116, line 11: is, read are.

Page 118, line 7: were, read was.

Page 119, line 7: were, read was.

Page 119, line 12: quartenary, read quaternary.

Page 119, line 15: quartenary, read quaternary.

Page 131, line 20: fit, read fits.

Page 131, line 21: CH_3H_7, read C_3H_7.

Page 132, line 23: preursor, read precursor

Page 127: 41 ⟶ 42, read