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STUDIES IN SESQUITERPENES – XLIX*
SESQUITERPENES FROM *FERULA JAESCHKEANA* VATKE (PART 1). JAESCHKEANADIOL – STRUCTURE, STEREOCHEMISTRY†‡

M. C. Sriraman, B. A. Nagasampagi, R. C. Pandey and Sukh Dev

National Chemical Laboratory, Poona 8, India

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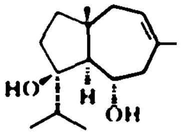
Abstract – A new sesquiterpene diol, now named jaeschkeanadiol, has been isolated from the roots of *Ferula jaeschkeana* Vatke and is shown to possess structure 1. Its stereochemistry has been established by a direct chemical correlation with laserol (9).

Ferula jaeschkeana Vatke is a perennial herb growing abundantly in Kashmir. When the stem of the plant is cut off, the remaining stump of the root stock exudes a milky sap which slowly dries to a brittle, brownish yellow resin, resembling asafoetida of commerce.[1,2] The present work was undertaken to examine the chemistry of extractives from the root stock, especially because it appeared to be a rich source of sesquiterpenoids, in view of the known[3] chemistry of asafoetida (*ex Ferula* spp.). It must be mentioned that the essential oil of the roots of *F. jaeschkeana* has been examined[4,5] and the presence of camphene,[5] α-pinene,[4,5] β-pinene,[5] Δ^3-carene,[5] limonene,[5] ( )-cadinene,[4] chamazulene[4] and S-guaiazulene[4] has been reported.

The roots on extraction, first with light petroleum and then with acetone furnish 7% and 6% of total extractables. Both the extracts have been found to be complex blends of several sesquiterpene alcohols, which occur chiefly as esters; besides, the light petroleum extract contains an essential oil to the extent of 16%. It has been possible to isolate five new sesquiterpene alcohols and one new azulene from these extracts. A sesquiterpene diol, m.p. 91–92°, $[\alpha]_D$ + 38·30°, which we name jaeschkeanadiol, is the major component of both the light petroleum and acetone extracts and we unfold below the evidence, which leads to its absolute stereostructure 1. The remaining sesquiterpenoids are all closely related to 1 and their structure determination will be reported subsequently.



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Jaeschkeanadiol structure. Jaeschkeanadiol analyses for $C_{15}H_{26}O_2$ (M^+-H_2O at m/e 220) and shows strong OH absorption (3350, 3280, 1040 and 978 cm^{-1}), but no C=O absorption in its IR spectrum. Its PMR spectrum reveals the following structural features: one $\rangle$C–Me (3H, s, 1·00 ppm), ·CH(<u>Me</u>)$_2$ (6H, a pair of doublets centred at 0·88 and 0·91 ppm, J = 7 Hz each), HC=C–<u>Me</u> (3H, broad s, 1·8 ppm), CHOH (1H, m, 3·8 ppm), C=CH (1H, an ill defined triplet, 5·4 ppm, J = 6 Hz). By D-exchange (PMR), presence of two hydroxyls is inferred and, this information coupled with the earlier data clearly shows that the compound must be a diol with one secondary and one tertiary hydroxyl. In confirmation of this, the compound on acetylation (Ac_2O, pyridine), at room temp (25°, 12 hr), furnished a monoacetate (m.p. 86–87°) with the required spectral characteristics: IR: OH 3550 cm^{-1}, OAc 1730, 1245 cm^{-1}; PMR: OAc (3H, s, 1·98 ppm), CHOAc (1H, m, 4·87 ppm).

On quantitative catalytic hydrogenation (PtO_2, AcOH), jaeschkeanadiol furnished a dihydro derivative (m.p. 92–93°, $M-H_2O^+$ at m/e 222) giving no coloration with tetranitromethane. Thus, jaeschkeanadiol is mono-olefinic and being $C_{15}H_{26}O_2$ must be bicyclic.

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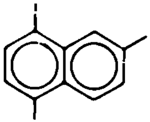
Jaeschkeanadiol failed to yield any appreciable amounts of aromatic products on S dehydrogenation (280°, 1·5 hr). However, on being exposed to Se at 290–295° (2 hr) the diol, yielded at least four aromatic compounds (TLC, silica gel-trinitrobenzene plates[6]), three of which could be obtained pure by preparative-layer-chromatography (PLC) on silica gel impregnated with trinitrobenzene (TNB)[6] Of these, one (major product) has been identified (m.p. of TNB complex, UV, IR, PMR, Mass) as daucalene (2)[7] The other two products are $C_{15}H_{18}$ azulenes, which have been characterized by their TNB complexes, UV, visible, PMR and mass spectra, and appear to be new.* Daucalene (along with azulenes of so far undetermined structure) is a typical dehydrogenation product of sesquiterpenes based on daucane (3) skeleton e g., carotol (4)[8,10], laserol[9] Thus, it is reasonable to assume that the bicyclic framework of jaeschkeanadiol is 3 This, as can be seen, answers eminently the structural requirements of the diol, as revealed by its PMR spectrum

Keeping in view the nature of the olefinic linkage (Me–C=CH–) of the diol, as well as the presence of an isopropyl group in the molecule, there are only two possible positions for the tert-OH (*viz* C_4 and C_{10}) on the framework 3 for jaeschkeanadiol Mass spectrum of the diol shows its base peak at *m/e* 195 (M^+–43) suggesting loss of isopropyl group, this ion further fragments by loss of water to *m/e* 177 (98%, M* at *m/e* 160·7) Similarly, the monoacetate shows M^+–C_3H_7 ion at *m/e* 237 (90%) and another ion at *m/e* 177 (100%) by further loss of AcOH (m* at *m/e* 132·2). This *facile* elimination of isopropyl group is best interpreted† in terms of tertiary OH being located at C_{10} Thus, jaeschkeanadiol can be represented by the partially defined structure 5

It has been possible to adduce chemical evidence in favour of 5, as well as to locate the secondary OH as follows Dihydrojaeschkeanadiol was oxidised with Jones reagent[12] to give an hydroxy ketone (IR OH 3400, 1020 cm^{-1}, C=O 1690 cm^{-1}), which on exposure to base (5% ethanolic KOH) underwent elimination of water to furnish an αβ-unsaturated ketone, $C_{15}H_{24}O$ (M^+, *m/e* 220) λ_{max} 256 nm (ε, 5500) IR C=O 1665 cm^{-1}, C=C 1600 cm^{-1} This transformation clearly establishes that hydroxyls are located 1,3 to each other Furthermore, the $\nu_{C=O}$ of the hydroxy ketone clearly shows that the CO function (and hence the original sec OH) must be located in the 7-membered ring. Further evidence in support of this was forthcoming when catalytic (5% Pd-C) hydrogenation of the αβ-olefinic ketone yielded a saturated ketone showing $\nu_{C=O}$ 1700 cm^{-1}. The PMR spectrum of the αβ-unsaturated ketone does not show any olefinic proton absorption, hence it must be represented by 6 These considerations lead to two possible gross structures 7 and 8, for jaeschkeanadiol

An incisive analysis of the CHOH signal in the PMR spectrum of the diol helps in deciding between the above two possibilities (7, 8) Though, in a spectrum taken in CCl_4, this signal occurs as a complex ill-defined multiplet (at 3·8 ppm), in a C_6H_6 soln spectrum this absorption appears as a well-defined triplet of doublets centred at 3·87 ppm (J_t = 10 Hz, J_d 5 Hz) This multiplicity (AB_2X) of the signal is consistent only with the formulation 8, which, then, must represent jaesch-



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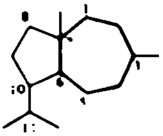

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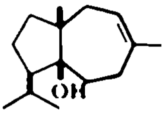

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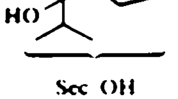

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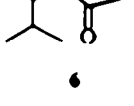

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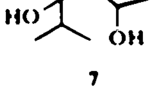

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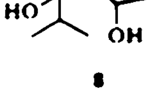

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*One of these azulenes (m p of TNB complex, 101–102°) may, in fact, be identical with an azulene (m p of TNB complex, 102°) of undetermined structure, reported[10a] as a product of Pd-C/Se dehydrogenation of carotol Structures of these azulenes will be discussed in a separate communication

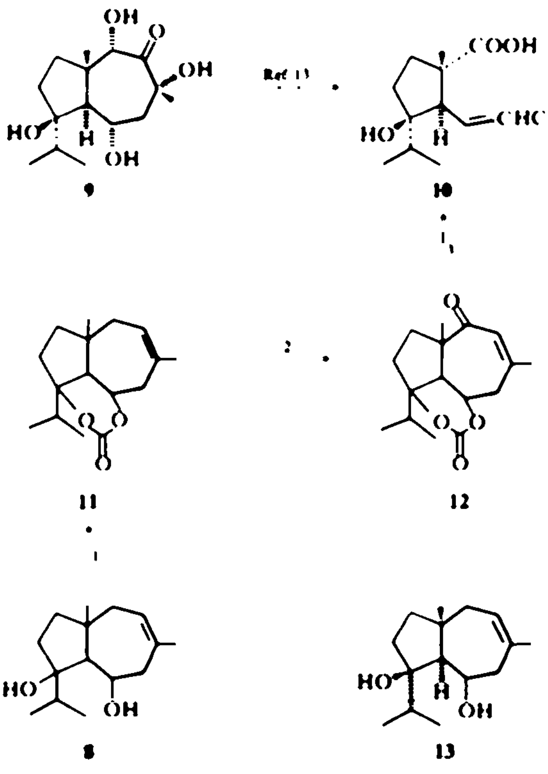
†This is based on the experience that in alcohols α-cleavage is an energetically favoured pathway[14] Also cf the electron impact-induced fragmentation of α-terpineol and terpen-4-ol[15]

keanadiol. This conclusion is also consistent with biogenetic considerations, briefly discussed later on and, is fully borne out by the chemical correlation described below.

Jaeschkeanadiol stereochemistry As can be seen from structure **8**, which has four asymmetric centres, the problem of elucidating its absolute stereochemistry can be quite involved. A simpler way of arriving at the absolute stereochemistry appeared to be to select a suitable daucane sesquiterpene of well-established stereostructure, for a direct chemical correlation. Laserol, a sesquiterpenoid from *Laserpitium latifolium* Linn has the absolute (?) stereostructure **9**, derived[13] from X-ray analysis of its *p*-bromobenzoate and the application[14] of benzoate rule.[15]* It has been possible to correlate jaeschkeanadiol with laserol through the common degradation product **10** (Fig 1).

Jaeschkeanadiol, on exposure to phosgene in presence of pyridine,[17] furnished, in almost quantitative yield, the carbonate **11**, m.p. 102–103° (M^+, m/e 264 IR O—CO—O[18] 1750, 1260, 1240 cm^{-1}); as expected the PMR spectrum of **11**, shows the C_5 proton (triplet of doublets) at 4·25 ppm, that is it suffers a downfield shift of 0·458 as compared to its signal in jaeschkeanadiol. Allylic oxidation of the carbonate was best effected with $Na_2Cr_2O_7$-AcOH in a two phase system when, a crystalline (m.p. 204–205°) $\alpha\beta$ unsaturated ketone (λ_{max} 234 nm, ϵ 12790, IR C=O 1670 cm^{-1}, C=C 1620 cm^{-1}, M^+, m/e 278) could be obtained, though in a low yield. That this compound has the desired structure **12** and is not the alternative -2-en-4-one or 3-en-2-one was clear from its PMR spectrum which still showed the C_5-proton signal as a complex multiplet ($W_{1/2}$ 20 Hz) at 4·70 ppm; besides, the olefinic proton signal now occurs as a broad singlet (5·91 ppm) as required by the structure **12**.

Oxidation of the unsaturated ketone to the targeted compound **10** could be effected efficiently by RuO_4, a reagent[19] used with considerable advantage for a similar degradation earlier.[20] Surprisingly, the product from this oxidation, which was ob-



Reagents
1 $COCl_2$, pyr.
2 $Na_2Cr_2O_7$, AcOH
3 RuO_4

Fig 1 Correlation of jaeschkeanadiol and laserol

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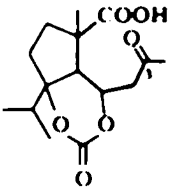
*The benzoate rule has certain limitations[16] and hence, it appears desirable to check the absolute stereochemistry by the application of 'benzoate sector rule'[18] or some other method.

tained after a work-up involving extraction with 5% Na_2CO_3 aq was straight-away the unsaturated keto acid **10**, rather than the carbonate **14**. Conceivably, β-elimination **15** is triggered by the presence of CO function at C_3 to furnish directly **10** with loss of CO_2.[21]



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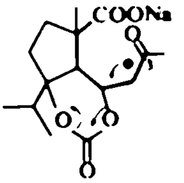

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The keto acid (**10**), thus obtained, was found to be identical in every respect (m.p., mixed m.p., $[\alpha]_D$, UV, IR, PMR and mass spectra) with a sample* of the acid prepared earlier by Sorm *et al.*[13] from laserol.

The correlation just described clarifies the relative (and absolute?) stereochemistry of all asymmetric centres in jaeschkeanadiol (**13**) except that at C_3. Configuration at C_3 was arrived at as follows. A study of molecular models (Dreiding) of the carbonate (**11**) corresponding to the two possible configurations at C_3 in **13** shows that both with C_3 α-OH or C_3 β-OH, the cyclic carbonate ring can be readily constructed and is strain-free (angle strain). However, the construction of this ring places further restraints on the number of preferred (energetics) conformations. An inspection of molecular models shows that depending on the configuration at C_3, there appears to be only one preferred conformation for each configuration (**16**, **17**). In these conformations the 7-membered ring has a chair-like conformation in which the bonds at C_1, C_2, C_7, C_6 and C_3 have quasi-axial/equatorial dispositions. The PMR spectrum of the carbonate shows the C_3-proton signal (at 4·25 ppm), as a triplet of doublets with $J_1 = J_3 = 10·5$ Hz and $J_2 = 5·5$ Hz. This pattern of lines is consistent only with **16**, which has two axial-axial-type and one axial-equatorial-type couplings.[22] Thus, jaeschkeanadiol can be assigned the stereostructure (absolute?) **18** (= **1**), which also represents its most probable conformation.

Table 1 summarises the relevant PMR spectral

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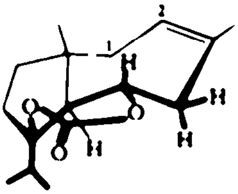
*Authors are grateful to Dr. M. Holub for an authentic sample of the acid **10** for direct comparison.

Table 1. PMR spectral characteristics of jaeschkeanadiol and its derivatives

			Chemical shift in ppm (J in Hz)†			
No	Compound	Solvent	$(Me)_2CH$	Me—C	C_3-Me	Other relevant signals
1	Jaeschkeanadiol (1)	CCl_4	2d, 0·88(7), 0·91(7)	s, 1·00	bs, 1·80	=C—CH, t*, 5·4(6), $C\underline{H}OH$, m, 3·8
2	Jaeschkeanadiol monoacetate	CCl_4	2d, 0·875(7), 0·9(7)	s, 1·03	bs, 1·83	=C—CH, t*, 5·4(6), $C\underline{H}OAc$, m, 4·86
3	Dihydrojaeschkeanadiol	CCl_4	2d, 0·9(7), 0·95(7)	s, 1·00	d, 1·00(7)	$C\underline{H}OH$, m, 4·1
4	β-Hydroxyketone (25)	CCl_4	d, 0·86(7)	s, 1·1	d, 1·10(6)	HO—C—C$\underline{H}$—CO, s, 2·6
5	α,β Unsaturated ketone (6)	CCl_4	d, 1·00(7)	s, 1·2	d, 1·1(7)	
6	Saturated ketone (26) (dihydro of 6)	CCl_4	2d, 0·74(7), 0·84(7)	s, 1·15	d, 1·1(7)	
7	Cyclic carbonate (11)	CCl_4	2d, 0·96(7), 1·025(7)	s, 1·08	bs, 1·81	=C—CH, t*, 5·4(6), CH—O—CO—O, m, 4·25
8	Keto carbonate (12)	$CDCl_3$	2d, 0·96(7), 1·06(7)	s, 1·33	bs, 2·05	=C—CH, bs, 5·91, CH—O—CO—O, m, 4·7
9	Keto acid (10)	$CDCl_3$	d, 0·99(7)	s, 1·4	s, 2·33	$\underline{H}$—C—C$\underline{H}$—C$\underline{H}$—C=O, 8 lines, ABX pattern, 3·08, 3·25, 6·03, 6·3, 6·76, 6·93, 7·03 and 7·2 ppm

†Chemical shift position given is that of the centre of the signal. Multiplicity abbreviations: s (singlet), d (doublet), t (triplet), 2d (two doublets), m (multiplet), b (broad), *(ill-defined).



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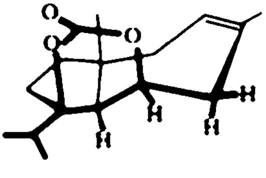

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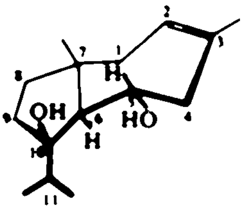

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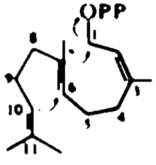
data of various compounds studied during this investigation

Biogenetic considerations. Biogenesis of sesquiterpenes of daucane class is considered[23] to involve a concerted *trans*-antiparallel cyclization of a suitably folded *cis*-farnesylpyrophosphate chain (19) to the ion 20, which, in principle, can be considered as the immediate precursor of daucane-based sesquiterpenoids. By a 1,2-hydride shift ion 20 can generate ion 21, which by OH



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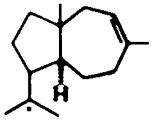

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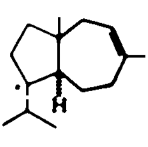

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take-up, followed by further oxidation at C_3 can give jaeschkeanadiol (1). It is heartening to know that in jaeschkeanadiol, ring-junction and the position of the olefinic bond are as expected on the basis of 21. Work is in progress to see if products resulting directly from the stabilization of cations 20/21 are present in *Ferula jaeschkeana*

It is of phylogenetic interest to note that, so far, all daucane-based sesquiterpenes have been isolated from four tribes, *Apieae*, *Peucedaneae*, *Laserpiteae* and *Dauceae* belonging to the subfamily *Apioideae* (Family *Umbelliferae*), which consists of a total of eight tribes.[24]

EXPERIMENTAL

All m ps and b ps are uncorrected, the former being determined on a Kofler hot stage. Light petroleum refers to the fraction b p 40-60°. All solvent extracts were dried over Na_2SO_4. Optical rotations were measured at room temp (27 ± 2°) in $CHCl_3$ on a Perkin-Elmer Polarimeter model 141.

UV spectra were taken on a Perkin-Elmer spectrophotometer, model 350, in 95% EtOH. IR spectra were recorded as smears (liquids) or Nujol mulls (solids), unless otherwise stated, on a Perkin Elmer Infracord model 137E. PMR spectra were taken in 10–20% soln in CCl_4 or $CDCl_3$ on a Varian A-60 spectrometer, signals are recorded in δ (ppm) relative to TMS as zero. Mass spectra were determined on a CEC mass spectrometer, model 21-110B using an ionizing voltage of 70 eV and a direct inlet system, besides the molecular ion, ten most abundant ions are given with their relative intensities.

Silica gel for column chromatography (−100, +200 mesh) was activated at 125–130°/6–8 hr and standardised.[27] TLC was carried out on 0·2 mm layers of silica gel containing 15% gypsum.

Isolation of jaeschkeanadiol. The roots of *Ferula jaeschkeana** (8·5 kg), which are quite fibrous, were cut into small pieces (2 cm length) and extracted in a Soxhlet apparatus first with light petroleum and then with acetone to yield respectively, a light petroleum extract (559 g, dark brown viscous liquid) and an acetone extract (509 g, dark brown gum). Both of these extracts are rich in jaeschkeanadiol and either of these may be processed for its isolation, of course the accompanying compounds are different in these two extracts. Procedure for the isolation of jaeschkeanadiol from acetone extract is given below.

The acetone extract (100 g) was dissolved in ether (1 litre) extracted with saturated $NaHCO_3$ aq (75 ml × 7) to remove free acids (6 g) in the usual manner and the residue (94 g) hydrolysed by refluxing with aq ethanolic KOH (5%, 1·5 litre) for 4 hr (N_2). This was worked up in the usual manner to give acidic (47 g) and neutral (47 g) portions.

The above neutral fraction was found (TLC, solvent 15% acetone in light petroleum) to be a mixture of at least five components, (R_{dye} 2·0, 0·9, 0·7, 0·4 and 0·2, R_{dye} is R_f relative to Sudan - III) of which one (R_{dye} 0·7) was major. This material (47 g) was chromatographed over SiO_2-gel-IIB (120 cm × 5·5 cm) with TLC monitoring.

Frac 1	light pet	0·305 g	Mixture containing azulene(s) R_{dye} 2·0
Frac 2	C_6H_6	5·28 g	Components with R_{dye} 0·9 and 0·7
Frac 3	Ether	36·0 g	Jaeschkeanadiol (major) R_{dye} 0·7 contaminated with minor components with R_{dye} 0·4 and 0·2

Frac 3 (35 g) was rechromatographed on SiO_2-gel/IIB (89 cm × 5·5 cm) and the fractions eluted with benzene were combined and recrystallised from light petroleum to furnish jaeschkeanadiol as snow-white needles, yield

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*The roots were collected from Kashmir and the authors are grateful to Dr C. K. Atal for the supply.

7.4 g, m.p. 91-92°, $[\alpha]_D$ +38.8° (*c*, 2%). Mass *m/e* 220 ($M-18^+$, 5%), 205 (6%), 195 (100%), 177 (98%), 159 (40%), 151 (55%), 123 (35%), 93 (32%), 55 (28%) and 41 (67%) (Found C, 75.51, H, 10.91 $C_{15}H_{26}O_2$ requires C, 75.51, H, 11.0%)

Its *monoacetate* (Ac_2O, pyridine, room temp/12 hr) was crystallised from light petroleum to afford silky needles, m.p. 86-87°, $[\alpha]_D$ +22.6° (*c*, 2%). Mass *m/e* 237 ($M-43^+$, 90%), 220 (20%), 177 (100%), 159 (97%), 134 (97%), 122 (95%), 93 (70%), 71 (50%), 55 (36%) and 43 (97%) (Found C, 72.95, H, 10.24 $C_{17}H_{28}O_3$ requires C, 72.82, H, 10.06%)

Dihydrojaeschkeanadiol Jaeschkeanadiol (2 g) was hydrogenated over prereduced PtO_2 catalyst (100 mg) in glacial AcOH (20 ml) at 25°/710 mm. Hydrogenation was complete after uptake of one molar equiv of H_2 (2 hr). Usual work up gave the required compound (2.05 g) which was recrystallised (light petroleum) to yield colourless crystals, m.p. 92-93°, $[\alpha]_D$ +30.73°, (*c*, 2.2%), IR OH 3300 cm^{-1}, mass *m/e* 222 ($M-18^+$, 6%), 204 (6%), 197 (50%), 179 (100%), 161 (37%), 137 (25%), 123 (35%), 95 (25%), 81 (35%) and 55 (23%) (Found C, 75.54, H, 11.42 $C_{15}H_{28}O_2$ requires C, 74.95, H, 11.74%)

Selenium dehydrogenation Jaeschkeanadiol (1 g) was heated with selenium (250 mg) at 280-295°/2 hr and the product on cooling was taken up in light petroleum (20 ml) and passed through a column of Al_2O_3 (Gr I, eluent light petroleum, 500 ml). The eluate on concentration gave a blue coloured liquid (0.640 g) which was found to be a mixture of at least four components (GLC: Aerograph model A-350 B, column 300 cm × 0.6 cm, 20% silicone SE 30 on Chromosorb W (60-70 mesh), temp 200°, H_2 30 ml/min). However, it showed three coloured spots on TLC (SiO_2-gel impregnated with 5% TNB[9]; solvent light petroleum, R_f 0.7 yellow, R_f 0.5 black and R_f 0.35 black). All the four components were separated by PLC on 5% TNB-impregnated SiO_2-gel[9] (solvent light petroleum, three irrigations) by cutting three fractions corresponding to the coloured bands and the fourth fraction corresponding to the colourless band towards the solvent front. Each of the four cuts of silica-gel layers was separately loaded as such on an Al_2O_3/I (10 cm × 1.5 cm) and eluted with light petroleum to give the following hydrocarbons

Frac 1	42 mg	daucalene (R_f 0.7)
Frac 2	10 mg	azulene I (R_f 0.5)
Frac 3	13 mg	azulene II (R_f 0.35)
Frac 4	225 mg	mixture containing non aromatic hydrocarbons (R_f 0.96)

Daucalene Frac 1 was distilled to give daucalene as a colourless liquid, b.p. 180-190° (bath)/10 mm; λ_{max} 322, 287, 231 nm (ε, 557, 5900, 59000 respectively); IR 1625, 1600 and 830 cm^{-1}; PMR $\underline{Me_2}CH$ (6H, d, 1.35 ppm, *J* = 7 Hz), two Ar-Me (two 3H singlets at 2.50 and 2.60 ppm), Ar-H (5H, m, 7-8 ppm). Mass *m/e* 198 (M^+ 65%), 183 (100%), 168 (13%), 165 (10%), 153 (10%), 141 (4%), 128 (4%), 113 (4%), 93 (3%) and 83 (4%)

Trinitrobenzene complex, yellow crystals from ethanol, m.p. 89-90°, mixed m.p. with an authentic sample (m.p. 89-90°) remained undepressed

Azulene-I Frac 2 was obtained as a blue coloured viscous liquid, λ_{max} 760, 621, 304, 288 and 281 nm (ε 24, 60, 603, 2777 and 3260 respectively)

Trinitrobenzene complex, black silky needles (EtOH), m.p. 101-102°; IR 1610, 1550 and 730 cm^{-1}; PMR $\underline{Me_2}CH$ (6H, d, 1.3 ppm, *J* = 7 Hz), two Ar-Me (6H, s, 2.51 ppm) and Ar-H (5H, m, 6.46-7.83 ppm). Mass (exclusive of the peaks of TNB moiety) *m/e* 198 (M^+, 100%), 183 (95%), 165 (39%), 153 (42%), 141 (20%), 128 (20%), 63 (35%), 51 (35%) and 39 (15%)

Azulene-II Frac 3 was distilled to furnish a blue coloured viscous liquid, b.p. 190-200° (bath)/10 mm; λ_{max} 710, 675, 637, 610, 585, 365, 348, 335, 286, 278 and 235 nm (ε 101, 134, 242, 267, 308, 1592, 3638, 2869, 23870, 24670 and 6365 respectively)

Trinitrobenzene complex, black feather-shaped needles from ethanol, m.p. 138-139°; IR 1610, 1540, 830 and 730 cm^{-1}; PMR $\underline{Me_2}CH$ (6H, d, 1.31 ppm, *J* = 7 Hz), two Ar-Me (6H, s, 2.52 ppm), Ar-H (5H, m, 6.6-7.41 ppm). Mass (exclusive of the peaks of TNB moiety) *m/e* 198 (M^+, 22.2%), 183 (9.2%), 156 (97%), 155 (100%), 141 (41%), 128 (11%), 115 (15%), 91 (49%), 75 (25%) and 63 (8.6%)

CrO_3 *Oxidation of dihydrojaeschkeanadiol* A soln of dihydrojaeschkeanadiol (1.39 g) in acetone (15 ml) was treated with Jones reagent[13] (prepared from CrO_3 6.68 g and conc H_2SO_4 5.75 ml, and diluted to 25 ml with H_2O) drop by drop at 15° till a permanent reddish brown colour persisted (3.2 ml). After 0.5 hr the excess reagent was destroyed (MeOH), the product diluted with water and extracted with ether. The ether soln was washed successively with 10% $NaHCO_3$ aq, water, brine and dried. The residue on concentration was purified by distillation to afford **25** (1.05 g) as a colourless oil, b.p. 146°/2 mm, $[\alpha]_D$ +106° (*c*, 2.1%) n_D^{30} 1.4710. Mass *m/e* 238 (M^+, 0.8%), 220 (1%), 195 (100%), 139 (15%), 119 (8%), 97 (12%), 69 (7%), 55 (12%), 43 (24%), 41 (9%) (Found C, 75.86, H, 11.26 $C_{15}H_{26}O_2$ requires C, 75.51, H, 11.0%)

αβ Unsaturated ketone (**6**) The above β hydroxy-ketone (1.4 g) was refluxed (N_2) with aq ethanolic KOH (5%, 30 ml) for 0.5 hr and the product (1.125 g) obtained after the usual work up was purified by passing through a column of SiO_2 gel (IIB, eluent C_6H_6) and distillation to furnish **6** as a colourless liquid, b.p. 145-155° (bath)/2 mm, $[\alpha]_D$ +84° (*c*, 2%), n_D^{30} 1.4900 (Found C, 81.37, H, 11.03 $C_{15}H_{24}O$ requires C, 81.76, H, 10.98%)

Saturated ketone (**26**) Hydrogenation of **6** (1.125 g) over 5% Pd-C (200 mg) in EtOH (135 ml) resulted in an uptake of 1 mole equiv of H_2 and the product obtained after the usual work up was distilled to give the required **26** (0.825 g) as a mobile liquid, b.p. 118°/2.5 mm, $[\alpha]_D$ 30° (*c*, 2%) n_D^{30} 1.4750 (Found C, 81.27, H, 11.74 $C_{15}H_{26}O$ requires C, 81.02, H, 11.79%)

Carbonate of jaeschkeanadiol (**11**) To a soln of jaeschkeanadiol (1.0 g) in $CHCl_3$ (50 ml) and pyridine (8 ml) maintained at 10° was added dropwise (10 min) with stirring a soln of 20% phosgene in toluene (20 ml)[14]. After the addition, stirring was continued for an additional 1 hr and the product left as such overnight (12 hr) at 0°. Excess phosgene was destroyed by the addition of ice-cold water (10 ml) and the product was extracted with ether. The ether extract was successively washed with 2N H_2SO_4 aq, 10% Na_2CO_3 aq, water, brine and dried. On evaporation of the solvent the solid carbonate obtained (1.185 g) was crystallised from light petroleum, m.p. 102-103°, $[\alpha]_D$ 41.62° (*c*, 2%). Mass *m/e* 264 (M^+, 15%), 220 (2%), 205 (4%), 177 (100%), 159 (63%), 151 (25%), 135 (27%), 123 (31%), 93 (30%) and 81 (23%) (Found C, 72.73, H, 9.23 $C_{16}H_{24}O_3$ requires C, 72.69, H, 9.15%)

Allylic oxidation of the carbonate. A mixture of **11** (1 g), $Na_2Cr_2O_7$ (3 g), AcOH (30 ml) and benzene (50 ml) was refluxed with continuous stirring for 85 hr. After cooling, it was diluted with water and extracted with ether. The ether soln was washed with 10% Na_2CO_3 aq, water, brine and dried. The residue obtained (0.650 g) after solvent evaporation was chromatographed over SiO_2 gel (IIB, 30 cm × 1.75 cm) and the fractions eluted with benzene were combined and crystallised (ether–light petroleum) to furnish **12**, 165 mg, as white crystals, m.p. 204–205°, $[\alpha]_D$ +16.28° (c, 2.25%). Mass *m/e* 278 (M^+, 4%), 263 (1%), 234 (4%), 191 (33%), 163 (20%), 145 (21%), 135 (25%), 123 (100%), 110 (19%) and 99 (36%). (Found: C, 69.21; H, 8.34. $C_{16}H_{22}O_4$ requires: C, 69.04; H, 7.97%.)

Keto acid (**10**). The above α,β-unsaturated ketone (50 mg) in acetone (20 ml) was oxidised by treating it with RuO_4 aq (prepared from black RuO_2, 20 mg, $NaIO_4$, 220 mg and H_2O 1 ml)[9,20] at 25° for 10 hr. During this period three lots of $NaIO_4$ (100 mg) in H_2O (1 ml) were added, each time the black ppt of RuO_2 was noticed. Finally, isopropanol (3 ml) was added, the contents stirred for 1 hr and the black ppt of RuO_2 filtered off and washed with acetone. The filtrate was concentrated, taken up in EtOAc and, the soln worked up for acidic (32 mg) and neutral (16 mg) portions in the usual manner. The acidic portion (32 mg) was crystallised from light petroleum to furnish the required **10** as colourless prisms, m.p. 121–122°, mixed m.p. with an authentic sample (m.p. 121–122°) remained undepressed. $[\alpha]_D$ +80° (c, 0.4%). λ_{max} 229 nm (ε, 12900). (Authentic sample $[\alpha]_D$ +82°, λ_{max} 229 nm, ε, 12800). IR: OH 3500 cm^{-1}, COOH 2700–2500, 1700 cm^{-1}; C=C–C=O 1675, 1625 cm^{-1}. Mass *m/e* 254 (M^+, 2%), 236 (2%), 211 (11%), 193 (10%), 175 (6%), 124 (46%), 123 (45%), 109 (55%), 81 (25%) and 43 (100%).

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