# Total Synthesis of the Sesquiterpene (−)-Daucene

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*Summary* (−)-Daucene (**11**) has been synthesized from (*R*)-(+)-limonene (**1**).

DAUCENE isolated from carrot seeds (*Daucus carota* L.) is a bicyclic sesquiterpene with the unique carotane skeleton.[1] An unusual mechanism for the biosynthesis of this skeleton has been proposed by Soucek.[2] We describe here the first synthesis of (−)-daucene (**11**).

Oxidation of (*R*)-(+)-limonene (**1**) {$[\alpha]_D^{20}$ +110° (*c* 1·16)[‡]} with peroxybenzoic acid in chloroform afforded the ex-

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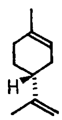
[‡] All rotations were measured for ethanolic solutions.

pected 1,2-monoepoxide (**2**) {$[\alpha]_D^{20}$ +32·3° (*c* 1·13)}, which was hydrolysed (1% $H_2SO_4$) to the crystalline 1,2-diol[3] (**3**) {$[\alpha]_D^{23}$ +16·3° (*c* 0·920)} [*ca.* 66% from (**1**)].

The crude ketoaldehyde (**4**) obtained by cleavage of diol (**3**) with $NaIO_4$ in tetrahydrofuran was cyclized in the presence of piperidine and acetic acid to give the αβ-unsaturated aldehyde (**5**) {$[\alpha]_D^{20}$ +21·4° (*c* 1·03)} [40% from (**3**)]. (**5**) was transformed into the dienone (**6**) {$[\alpha]_D^{27}$ +44·7° (*c* 0·974)} (37%) on treatment with acetone and 3N-NaOH.[4]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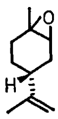
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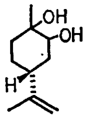
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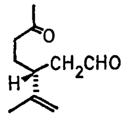
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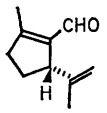
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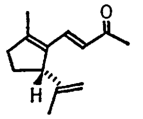
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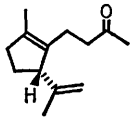
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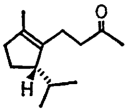
Treatment of (**6**) with sodium and ethanol followed by oxidation by Jones procedure gave the desired ketone (**7**) {$[\alpha]_D^{28}$ +85·9° (*c* 0·920)}, but in less than 5% yield. The αβ double bond in the ketone (**6**) was found to be saturated selectively by reduction with triphenyltin hydride[5] in refluxing toluene for 4 h (81% yield).

Treatment of the ketone (**8**) {$[\alpha]_D^{27}$ −14·0° (*c* 0·784)}, prepared by catalytic hydrogenation [Pd–C (10%) in EtOH] of (**7**), with sodium acetylide in liquid ammonia yielded the acetylenic carbinol (**9**) {$[\alpha]_D^{29}$ +6·45° (*c* 0·954)}, which was then hydrogenated selectively (Lindlar catalyst in hexane) to the corresponding allylic alcohol (**10**) {$[\alpha]_D^{28}$ −3·65° (*c* 1·00)} [57% from (**7**)].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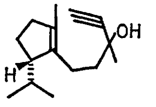
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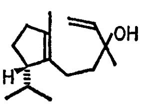
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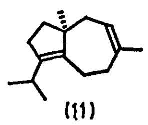
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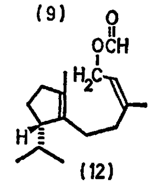
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Acid-catalysed cyclization of the allylic alcohol[6] (**10**) with formic acid for 10 min at room temperature gave 5 compounds, which were separated by chromatography on silica gel in yields of 42, 20, 16,§ 15, and 7%. The main component was further purified by preparative t.l.c. on 10% $AgNO_3$–$SiO_2$, and identified as (−)-daucene (**11**) {$\nu_{max}$ 830 cm$^{-1}$; δ 0·92 (3H, d, *J* 5 Hz), 0·99 (3H, d, *J* 5 Hz), 0·94 (3H, s), 1·73 (3H, s, $W_{\frac{1}{2}}$ 4 Hz), and 5·37 (1H, t, *J* 5 Hz) p.p.m.; $[\alpha]_D^{21}$ −21·5° (*c* 0·752); *m/e* 204 ($M^+$)} by comparison with an authentic sample prepared from natural carotol.[7]

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§ The n.m.r. spectra of one of the components (16%) was consistent with structure (**12**) but the other three products were not identified.

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