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STUDIES IN TERPENOIDS—XVII[1]

SYNTHESIS OF 7-HYDROXYCADALENAL AND SOME RELATED NATURALLY OCCURRING SESQUITERPENOIDS*[1]

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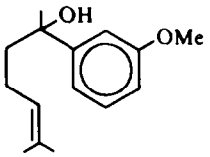
Abstract—The synthesis and facile elaboration of 7-methoxycalamenal (**4b**) to four naturally occurring phenolic sesquiterpenoids, 7-hydroxycalamenene (**4e**), 7-hydroxycadalene (**13e**), 7-hydroxycalamenal (**4f**), and 7-hydroxycadalenal (**13f**) are described.

ROWE *et al.*[2] and Lindgren and Svahn[3] recently reported the isolation of phenolic sesquiterpenoids of cadinene skeleton from the elm woods, *Ulmus rubra* Mühl and *Ulmus glabra* Huds. The present communication describes the synthesis of four members of this group, (i) 7-hydroxycalamenene (**4e**), (ii) 7-hydroxycadalene (**13e**), (iii), 7-hydroxycalamenal (**4f**) and (iv) 7-hydroxycadalenal (**13f**), the last two for the first time.

Grignard reaction of *m*-bromoanisole with 6-methylhept-5-ene-2-one gave a mixture of the carbinol (**1**) and its dehydration product (**2**). Catalytic hydrogenolysis[4]/hydrogenation (10% Pd/C or PtO_2 in acetic acid containing perchloric acid) of this mixture failed to furnish **3**. However, reduction to **3** was effected by lithium in moist liquid ammonia.[5] The polyphosphoric acid (PPA) cyclisation of **3** to the 7-methoxytetralin (**4a**) was patterned after similar successful results achieved by Bardhan and Mukherji[6] with monocyclic carbinol precursors of compounds of type **5** and our own experience[7] in the cyclisation of *ar*-curcumene (**5**) to calamenene (**6**).[8] However, since the unsymmetrical substitution of the ring in **3** and the more stable tertiary cationic site of the side chain does not preclude other products of cyclisation **7–9** besides **4a**, it was considered desirable to establish the structure of **4a** by an alternate synthesis.

4-(*p*-Anisyl)-5-methylhexanoic acid (**10**),[9] obtained by the inverse Grignard addition[10] of isopropylmagnesium iodide to methyl 3-(*p*-anisoyl)-propionate[11] followed by hydrogenation,[12] was cyclised by PPA under mild conditions[13] to the tetralone **11**. Reaction of **11** with methyllithium and hydrogenolysis of the resulting carbinol (**12**) gave the corresponding 7-methoxytetralin (**4a**), the IR spectrum of which compared favourable with that of **4a** prepared by the preceding shorter procedure. Minor differences noticed in the fingerprint region of the two spectra may be attributed to the existence in minor amounts of the other possible cyclic isomers **7–9** in the product obtained by the former route and a likely higher *cis/trans* ratio[14] of **4a** as a result of catalytic hydrogenation in the product from the latter synthesis. The methoxytetralin (**4a**) from both the routes on formylation by Vilsmier reaction[15] gave identical 7-methoxycalamenal (**4b**) isolated as the spraringly soluble (ethyl acetate) semicarbazone

*[1] The subject matter of this paper was presented at the Indian Institute of Technology, Madras on June 13,1970.



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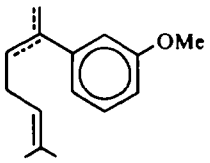

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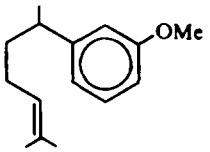

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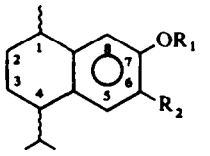
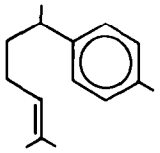


4a: $R_1 = Me$; $R_2 = H$



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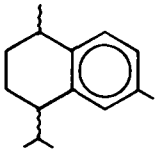

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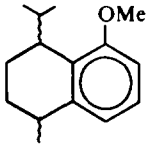

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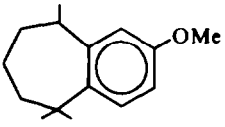

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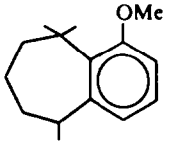

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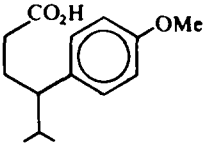

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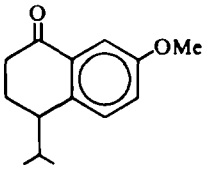

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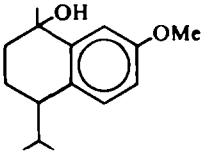

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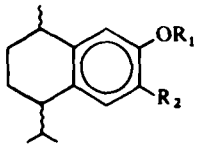
(**4c**), although the yield (42%) from the tetralin by the latter route was better. The semicarbazone was repeatedly crystallized to constant m.p. (207–208°) and this pure crystalline material was used in all its subsequent conversions. That C-6 is the favoured position for formylation was established by Buu-Hoi *et al.*,[16] in the analogous case of 6-methoxy-1,2,3,4-tetrahydronaphthalene. The subsequent conversions of **4b** confirmed that formylation did indeed occur in the desired position.

Wolff-Kishner reduction of the semicarbazone[17] **4c** gave 7-methoxycalamenene (**4d**) in high yield. Demethylation of **4d** by pyridine hydrochloride[18] furnished the phenol, 7-hydroxycalamenene (**4e**), the infrared spectrum of which was identical in all respects with the authentic spectrum[*2] of the naturally occurring material. It gave a crystalline 3,5-dinitrobenzoate in excellent yield, m.p. 146° (Rep.[19] m.p. 146°). 7-Hydroxy-

[*2] We are deeply grateful to Dr. J. W. Rowe of the Forest Products Laboratory, Madison, Wisconsin for authentic IR spectra of the naturally occurring phenolic sesquiterpenoids **4e**, **4f**, **13e**, **13f** and for an authentic specimen of **13f**.

calamenene was obtained earlier by de Mayo *et al.*[20] as a degradation product of copaene and was synthesized by Cocker and Sainsbury[19] from *o*-cresol methyl ether in ten steps.

The above pure semicarbazone **4c** was used for the regeneration[21] of the parent 7-methoxycalamenal (**4b**) which in turn was demethylated to 7-hydroxycalamenal (**4f**) and purified *via* the semicarbazone. Its infrared spectrum was identical in all respects with authentic spectrum.*[2]



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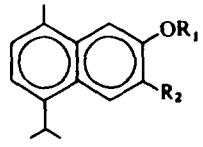

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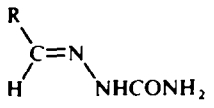
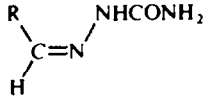
a: R_1 = Me; R_2 = H
b: R_1 = Me; R_2 = CHO
c: R_1 = Me; R_2 = CH=NNHCONH$_2$
d: R_1 = R_2 = Me
e: R_1 = H; R_2 = Me
f: R_1 = H; R_2 = CHO

Dehydrogenation of **4c** was effected using dichlorodicyanoquinone[22] (DDQ). Repeated crystallization (ethyl acetate) of the product gave the semicarbazone **13c** as a crystalline solid, m.p. 209°. Its mixed melting point with **4c** was depressed and the infrared spectrum differed markedly from that of **4c**. However, the melt of **13c** resolidified on further heating and the solid remelted at 275–276° (with decomposition). This behaviour may be attributed to the thermal isomerisation of one geometric isomer to the other (**A**→**B** or *vice versa*).



A



B

The Wolff-Kishner reduction of **13c** to 7-methoxycadalene (**13d**) followed by demethylation furnished 7-hydroxycadalene (**13e**), m.p. 118°, identical with the reported value.[23] Its infrared spectrum in carbon tetrachloride was identical in all respects with the authentic spectrum of the natural product.*[2] This phenolic cadalene (**13e**) was synthesized recently by Gallagher and Sutherland[23] starting from (+)-carvone in a six step sequence, during the course of a synthetic programme designed to furnish authentic hydroxycadalenes required for structural correlations of natural products. In the above Wolff-Kishner reduction of **13c** to the liquid 7-methoxycalamenene (**13d**), a small

amount of a solid also sublimed along with the major liquid product (**13d**). From the hydroxyl bands [3546 (O—H), 1238 cm^{-1} (C—OH)] in the IR spectrum of the impure solid (not melting below 100°). it is believed to be the naphthol **13e** (m.p. 118°) arising from concurrent ether cleavage under the strong alkaline conditions of Wolff–Kishner reduction. Alkali promoted phenol ether cleavage has been reported in literature.[18] However, complete characterisation of the solid sublimate was not attempted owing to its very small amount.

From the semicarbazone (**13c**), m.p. 209°, the crystalline 7-methoxycadalenal (**13b**) was regenerated. Its demethylation with pyridine hydrochloride furnished 7-hydroxycadalenal (**13f**) as brilliant yellow needles, m.p. 88°. Its identity with the natural sample*[2] (m.p. 88°) was established by mixed melting point and comparison of infrared spectra. It gave a crystalline pale yellow phenylhydrazone, m.p. 186° (reported[2] for the natural sample, m.p. 186°).

The versatility of 7-methoxycalamenal (**4b**) has thus been amply demonstrated in its facile conversion to four naturally occurring phenolic sesquiterpenoids. Further transformations of 7-hydroxycalamenene (**4e**) and 7-hydroxycadalene (**13e**) to mansonones A, B and C[24] are in progress in our laboratories.

EXPERIMENTAL*

2-(3-*Anisyl*)-6-*methylhept*-5-*en*-2-*ol* (**1**). To a suspension of Grignard reagent prepared from *m*-bromoanisole (89 g) and magnesium (11·42 g) in anhyd ether (225 ml) was added with stirring a soln of 6-methylhept-5-ene-2-one (60 g) in thiophene-free dry benzene (100 ml). After stirring for 0·5 hr, the ether was distilled off till the distillation temp rose to 76°. Benzene (100 ml) was added and stirring and refluxing continued for 4·5 hr. It was left overnight and decomposed with cold NH_4Cl aq. Extraction followed by distillation furnished with partial dehydration, a product consisting of **1** and **2** (63·4 g, >57%), b.p. 148–150°/2·5 mm; ν_{max}^{film} 3468 (O—H), 1678 (C=O), 1608, 1593, 1498 (aromatic), 783 cm^{-1} (1,3-disubstituted benzene).

2-(3-*Anisyl*)-6-*methylhept*-5-*ene* (**3**). Lithium pieces (15 g) were added in 0·5 hr with stirring to the above mixture in anhyd ether (50 ml), liq NH_3 (~2 l) and water (18 ml). After another 0·5 hour's stirring, solid NH_4Cl (~50 g) was added to discharge the blue colour. Ammonia was driven off and water (150 ml) added. Extraction with light petrol and distillation of the residue gave **3** (55·3 g, 93·7%), b.p. 110–112°/1·5 mm; λ_{max}^{EtOH} 271, 278 nm (ε = 1497, 975); ν_{max}^{film} 1672 cm^{-1} (C=C). (Found: C, 82·7; H, 10·1. $C_{15}H_{22}O$ requires: C, 82·5; H, 10·2%).

1-*Methyl*-4-*isopropyl*-7-*methoxytetralin* (**4a**). (a) To polyphosphoric acid (210 g) [from P_2O_5 (98 g) and H_3PO_4 (63 ml)] **3** (25 g) was added and heated (170–180° b.t.) with stirring (0·5 hr). The mixture was cooled, poured into ice-water and extracted with ether. The ether extract was washed, dried and evaporated. The residue furnished a distillate (16·2 g, 64·8%) b.p. 118–122°/3 mm; λ_{max}^{EtOH} 278, 285 nm (ε = 2901, 1585); ν_{max}^{film} 1619, 1588, 1508 (aromatic), 1388, 1372 (isopropyl), 824 cm^{-1} (1,2,4-trisubstituted benzene). (Found: C, 82·9; H, 9·8. $C_{15}H_{22}O$ requires; C, 82·5; H, 10·2%). (b) *Vide infra* for alternate preparation.

4-*Isopropyl*-7-*methoxytetralone* (**11**). 4-(*p*-Anisoyl)-5-methylhexanoic acid[9–12] (**10**, 30·7 g) was stirred at 60° (b.t.) with PPA (90 g) [prepared from P_2O_5 (52 g) and H_3PO_4 (27 ml)] for 5 mts. It was kept aside (10 mts) and poured into ice-water. The crude tetralone (22 g, 78·3%) obtained on work-up was steam distilled (sluggish) over NaOH aq (5%). Distillation furnished the pure tetralone (**11**, 14·2 g, 50·2%); b.p. 140–145°/1·5 mm; λ_{max}^{EtOH} 223, 256, 318–225 nm (ε = 17160, 6976, 2520); ν_{max}^{film} 1692 (C=O), 1617, 1574, 1502 (aromatic), 1372, 1391 cm^{-1} (isopropyl); $n_D^{23·5}$ 1·5570. (Found: C, 77·0; H, 8·6. $C_{14}H_{18}O$ requires: C, 77·0; H, 8·3%).

* All m.ps are uncorrected. IR spectra were taken on Carl–Zeiss UR-10 instrument. UV measurements were made on Unicam SP-700 or Carl-Zeiss VSU-2 instrument. Bath temp. (b.t.) are given for sublimations. Before removal of solvents the extracts were appropriately washed (neutral where necessary) and dried (Na_2SO_4). Light petrol refers to a fraction boiling between 40–65°.

2,4-*Dinitrophenylhydrazone*, m.p. 176–177° (EtOAc–EtOH). (Found: N, 14·2. $C_{20}H_{22}N_4O_5$ requires: N, 14·1%).

1-*Methyl-4-isopropyl-7-methoxytetralol*-1 (**12**). An ethereal soln (~175 ml) of MeLi prepared from MeI (23·0 g) and Li wire (2·5 g) in the usual way was filtered through glass wool in N_2 atm and added dropwise with stirring and cooling to a soln of the tetralone **11** (17 g) in ether (50 ml). After reflux (2 hr) it was left overnight and decomposed with cold water. The crude carbinol (17·95 g) showed slight contamination with the starting ketone; ν_{max}^{film} 3430 (O—H), 1692 cm^{-1} (shoulder, C=O).

1-*Methyl-4-isopropyl-7-methoxytetralin* (**4a**). The above carbinol was hydrogenolysed over Pd/C (10%, 1·7 g) in AcOH (150 ml) containing $HClO_4$ (70%, 1·5 ml) till the absorption of H_2 ceased. The catalyst was filtered off and the filtrate concentrated (~25 ml). It was diluted with water and extracted with ether. The impure tetralin **4a** (15·4 g) carrying the contaminant **11** was treated with 2,4-dinitrophenylhydrazine reagent in EtOH. The precipitated 2,4-dinitrophenylhydrazone was filtered off. The filtrate after removal of EtOH was steam distilled to furnish pure **4a** (11·0 g, overall yield based on tetralone **11**, 61·3%).

7-*Methoxycalamenal semicarbazone* (**4c**). To Vilsmier reagent from $POCl_3$ (6·5 g) and DMF (2·9 g) at 0° was added with stirring the tetralin **4a** (6·54 g). The reaction mixture was heated (90–100°, b.t.) with stirring (5 hr). It was cooled, satd NaOAcaq (50 ml) was added and boiled (5 min). Work up furnished a mixture (6·4 g) of the aldehyde and the unreacted starting material. It was directly converted into the semicarbazone (in presence of pyridine). The sticky solid was extracted with EtOAc. The extract after washing, drying and concentration, deposited a slightly coloured semicarbazone **4c** (3·85 g, 42·4%), m.p. 198–203°. Two successive crystallizations gave a pure sample, m.p. 207–208°. An analytical sample melted at 208° (EtOAc). (Found: N, 14·0; $C_{17}H_{25}N_3O$ requires: N, 13·9%). The yield and purity of the semicarbazone was found to be variable. The sample of tetralin **4a** obtained by the cyclisation of **3** gave poorer yields of the semicarbazone.

7-*Methyoxycalamene* (**4d**). The above semicarbazone **4c** (1·82 g) was refluxed (6 hr) with a soln of KOH (4·5 g) in water (2 ml) and ethylene glycol (30 ml). It was cooled, acidified with dil HCl (1:1), diluted with water (200 ml) and extracted with ether. The product **4d** (1·45 g) was purified by chromatography (SiO_2, 45 g). Light petrol eluted the 7-methoxycalamenene (1·29 g, 92·8%), b.t. 111°/1·5 mm; $\lambda_{max}^{heptane}$ 224, 236, 281, 286 nm (ε = 1615, 4480, 2451, 2403); ν_{max}^{film} 1621, 1580, 1499 (aromatic), 1387, 1374 cm^{-1} (isopropyl); n_D^{24} 1·5350 (Found: C, 82·7; H, 10·0. $C_{16}H_{24}O$ requires: C, 82·8; H, 10·4%).

7-*Hydroxycalamenene* (**4e**). A mixture of pyridine hydrochloride (10 g) and **4d** (0·5 g) was refluxed under N_2 for 3 hr. It was cooled, diluted with 2N HCl and extracted with ether. The demethylated oily product*[3] (0·49 g) was purified by chromatography (SiO_2, 7 g). The methyl ether **4d** was removed by light petrol while the phenolic compound was eluted with benzene (0·41 g, 87%), b.t. 125–130°/1·5 mm; λ_{max}^{EtOH} 283 nm (ε = 2787) [Lit.[19] λ_{max}^{EtOH} 283 nm (log ε 3·6)]; ν_{max}^{film} 3400 (O—H) 1619, 1593, 1511 (aromatic), 1388, 1371 (isopropyl), 1192 cm^{-1} (C—OH). (Found: C, 82·0; H, 10·0. $C_{15}H_{20}O$ requires: C, 82·5; H, 10·1%).

3,5-*Dinitrobenzoate*, needles m.p. 146° after repeated crystallizations from EtOH.

7-*Methoxycalamenal* (**4b**). The semicarbazone **4c** (0·8 g) was refluxed with stirring with oxalic acid aq (25%, 50 ml) and *n*-heptane (50 ml) under N_2 atm till the solid suspension disappeared (~3 hr). It was cooled and the pure aldehyde **4b** extracted (0·72 g), b.t. 140°/2 mm. It solidified on keeping, m.p. 80–81° (light petrol), $\lambda_{max}^{heptane}$ 222, 228, 258, 263, 320, 326 nm (ε = 21180, 20720, 13450, 11900, 4465, 4373); ν_{max}^{film} 2772 (C—H of aldehyde), 1697 (C=O), 1622, 1520 cm^{-1} (aromatic). (Found: C, 78·1; H, 8·8. $C_{16}H_{22}O_2$ requires: C, 78·0; H, 9·0%).

7-*Hydroxycalamenal* (**4f**). The above methoxy compound **4b** (0·48 g) was heated with pyridine hydrochloride (20 g) at 170–180° for 3 hr under N_2 atm. The residue obtained on work up*[3] was sublimed (b.t. 130–135°/1·5 mm) and the sublimate was converted into the *semicarbaone* (0·55 g, m.p. 175–183°). One crystallization from EtOAc raised the m.p. to 185–186° (250 mg). Oxalic acid regenerated from this the pure aldehyde **4f** (b.t. 130–135°/1·5 mm; $\lambda_{max}^{heptane}$ 221, 229, 233, 263, 269, 342 nm (ε = 25610, 30030, 29830, 23820, 27010, 8078) [Lit.[2] $\lambda_{max}^{isooctane}$ 220, 228, 231, 262, 268, 297, 309, 339 nm (log ε 4·53, 4·56, 4·54, 4·40, 4·45, 3·69, 3·82, 3·88)]; ν_{max}^{film} 3238 (O—H), 2767 (C—H of aldehyde), 1672 (C=O), 1611, 1591, 1537 (aromatic), 1194 cm^{-1} (C—OH); n_D^{24} 1·5660 (Found: C, 77·4; H, 9·0. $C_{15}H_{22}O_2$ requires: C, 77·6; H, 8·7%).

Attempted demethylation of **4b** at the refluxing temp of pyridine hydrochloride gave a phenolic compound (b.t. 140–150°/2 mm); ν_{max}^{film} 3340 cm^{-1} (O—H). However, it did not show any CO absorption.

*[3] The 7-hydroxycalamenene (**4e**) and other phenolic sesquiterpenoids reported in this work are not quantitatively extractable from the organic phase with NaOH aq.[25]

7-Methoxycadalenal semicarbazone (**13c**). The semicarbazone **4c** (3·38 g) in warm dioxan (100 ml) was treated with DDQ (5·7 g) and allowed to stand for 3 hr. The dioxan was removed *in vacuo* and the residue taken up in NaOH aq (2·5%, 200 ml) was extracted (EtOAc). The residue (2·8 g) was crystallized (EtOAc) to constant m.p., m.p. 209° (1·95 g). An analytical sample of **13c**, m.p. 209°, solidified as the heating was continued and melted again with decomposition at 275–276° (Found: N, 13·7. $C_{17}H_{21}N_3O_2$ requires: N, 14·0%).

7-Hydroxycadalene (**13e**). The semicarbazone **13c** (0·25 g) was refluxed with a soln of KOH (4·5 g) in water (2 ml) and diethylene glycol (30 ml) for 3 hr. After work up*[3] as for **4d**, the residue (0·22 g) was sublimed (b.t. 115–120°/1·5 mm). Since it was contaminated with phenolic compound formed by demethylation of the methyl ether, it was subjected to pyridine hydrochloride demethylation as described previously. The phenol **13e** (0·19 g) sublimed at 140°/1·5 mm, m.p. 110°. Three successive crystallizations from light petrol gave pure **13e**, m.p. 118°)Rep.[23] m.p. 118–119·5°); $\lambda_{max}^{heptane}$ 224, 238, 285, 292, 297, 315, 329 nm (ε = 272630, 27830, 7775, 3668, 3668, 1223, 1525), λ_{infl} 264, 274, 303 nm (ε = 2525, 2670, 2293) [Rep.[23] $\lambda_{max}^{isooctane}$ 222; 238, 285, 293, 297, 317, 331 nm (log ε 4·56, 4·56, 3·68, 3·64, 3·65, 3·26, 3·34)]; λ_{infl} 266, 275, 304 nm (log ε 3·32, 3·53, 3·30); $\nu_{max}^{CCl_4}$ 3622 (O—H), 1641, 1612 (aromatic), 1389, 1371 (isopropyl), 1221 cm^{-1} (C—OH) (Found: C, 84·5; H, 8·7. $C_{15}H_{18}O$ requires: C, 84·1; H, 8·5%).

7-Methoxycadalenal (**13b**). 7-Methoxycadalenal semicarbazone (**13c**, 1 g) on regeneration using oxalic acid aq as described earlier, furnished **13b** (0·78 g), solidifying (m.p. 67–70°) on sublimation (b.t. 140–145°/2 mm). Two successive crystallizations from light petrol gave the analytical sample, m.p. 71° [Rep[2] m.p. 78·5°]; $\lambda_{max}^{heptane}$ 220, 250, 261, 302, 314, 370 nm (ε = 24650, 36290, 25690, 8570, 9874, 2564); ν_{max}^{KBr} 2772 (C—H of aldehyde), 1697 (C=O), 1622, 1520 cm^{-1} (aromatic). (Found: C, 79·1; H 7·5. $C_{16}H_{18}O_2$ requires: C, 79·3; H, 7·5%).

7-Hydroxycadalenal (**13f**). The methoxyaldehyde **13b** (0·29 g) was refluxed gently with pyridine hydrochloride (10 g) for 1·5 hr. Work up*[3] followed by sublimation (b.t. 140°/1·5 mm) gave **13f** (0·23 g); m.p. 77–79°. Crystallization from light petrol gave pure **13f**, m.p. 81°. On admixture with an authentic sample (m.p. 88°) the mixture melted at 87–88°. However, crystallization of the synthetic specimen of **13f** with a seed of the authentic material*[2] converted it entirely into the higher melting variety (m.p. 88°); $\lambda_{max}^{heptane}$ 220, 256, 266, 303, 313, 390 nm (ε = 31880, 37690, 36090, 9270, 10480, 2429), [Rep.[2] $\lambda_{max}^{isooctane}$ 221, 256, 266, 303, 314, 397 nm (log ε 4·44, 4·58, 4·59, 3·98, 4·03, 3·41)], ν_{max}^{KBr} 3238 (O—H), 2767 (C—H of aldehyde), 1672 (C=O), 1611, 1591, 1537 (aromatic), 1194 (C—OH). (Found: C, 78·9; H, 7·3. $C_{15}H_{16}O_2$ requires: C, 78·9; H, 7·1%).

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