Addition of a Functionalized Isoprene Unit to an Allyl Alcohol. Part II.¹ Reactions with Furylmethanol and Thienylmethanol and Synthesis of Torreyal and Dendrolasin.²

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The double bond in the furan and thiophen ring can be induced to participate in a Claisen-Cope-type rearrangement. Furans substituted in the 2-position react more readily than those substituted in the 3-position. The 2-methylbuta-1,3-dienyl ether of 3-furylmethanol can, however, be made to rearrange thermally, and the aldehyde thereby obtained can be converted into the corresponding alcohol, and then, by a second Claisen-Cope reaction to torreyal. The related sesquiterpenes, neotorreyol and dendrolasin and the monoterpene perillene have been synthesized.

WE have given ¹ a general description of the double Claisen-Cope reaction as applied to aliphatic allyl alcohols and in particular to 2-methyl-6-methylenocta-2,7-dienol; β -sinensal has been synthesized by application of the latter reaction.³ Here we report the application of the reaction to 2- and 3-furylmethanol and to 2-thienylmethanol. It could not be anticipated without doubt that 2-furylmethanol alcohol would react under the conditions of this reaction; its vinyl ethers are reportedly stable.4 *

RESULTS AND DISCUSSION

Treatment of 2-furylmethanol (1) with 1-ethoxy-2methylbuta-1,3-diene (2)⁵ in the presence of mercuric acetate gave two products in the ratio 9:1; the major product was the chain-extended aldehyde (3). The second compound was also an aldehyde, the n.m.r. spectrum of which clearly indicated a disubsituted furan, two methyl groups, one of which was attached to the furan and the other to a quaternary carbon atom, and a vinyl group not conjugated with the aldehyde. This compound, assigned structure (4), was thought to arise from the intermediate (b), after the first Claisen rearrangement, by a 1,3-hydrogen shift (see Scheme). The mass spectrum of the compound indicated loss of the CHO radical to give an ion at m/e 135, which supports our assignment; this evidence would not support a structure with a furylmethyl group (see below). Similar treatment of 2-thienylmethanol gave 2-methyl-5-(2thienyl)pent-2-enal (5) as the main product. We have shown¹ that the main product from reaction of an allyl alcohol and 1-ethoxybutadiene, is not generally the result of a double rearrangement, but of a single Claisen rearrangement followed by a 1,3-hydrogen shift to yield an $\alpha\beta$ -unsaturated aldehyde.^{1,6,7} This is not true for furylmethanol.

Treatment of the alcohol with 1-methoxybutadiene in the presence of mercuric acetate gave a mixture of compounds and, since these were likely to be thermally unstable, they were purified by t.l.c. Unfortunately, one of the compounds tended to decompose on silica gel but, nevertheless, it was possible to separate roughly three fractions by liquid phase chromatography. The compound with the shortest retention time was identified



as the ether (6). Comparison of the n.m.r. spectrum of this compound with the spectra of cis- and trans-1ethoxybutadiene⁸ showed that only the trans-ether was present; the spectral region having the butadiene signals was closely similar to that of trans-ethoxybutadiene, signals corresponding to the *cis*-isomer being absent. The middle zone of the chromatogram contained the acetal (7), which was purified by gas chromato-Although it decomposed on silica gel, graphy. careful rechromatography of this fraction on this absorbent gave a small amount of an aldehyde fraction. Gas chromatography separated this into 5-(2-furyl)pent-

⁴ W. H. Watanabe and L. E. Conlon, J. Amer. Chem. Soc., 1957, **79**, 2828; U.S.P. 2,760,990, Aug. 28, 1956. ⁵ I. N. Nazarov, S. M. Makin, and B. Kruptsov, Zhur. obshchei Khim., 1959, **29**, 2079. ⁶ A. E. Thomas, Chimia, 1967, 504

A. F. Thomas, Chimia, 1967, 594.

⁷ This type of reaction was already described by S. Julia, M. Julia and H. Linarès, Bull. Soc. chim. France, 1962, 1960.

J. M. Bell, R. Garrett, V. A. Jones, D. G. Kubler, J. Org. Chem., 1967, 32, 1307.

^{*} We are at present investigating the thermal stability of vinyl ethers of furylmethanol, and find them to rearrange at higher temperatures.

¹ Part I, A. F. Thomas, J. Amer. Chem. Soc., 1969, 91, 3281. ² Preliminary communication, A. F. Thomas, Chem. Comm., 1968, 1657.

³ A. F. Thomas, *Chem. Comm.*, 1967, 947. Since the appearance of this note, K. A. Parker and W. S. Johnson (*Tetrahedron* Letters, 1969, 1329) have published a different synthesis of dendrolasin.

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2-enal (8) and 2-(2-methyl-3-furyl)but-2-enal (3:1), only one isomer of each apparently being present. Although an acetal is presumably formed during the reaction with 2-methylbutadiene ethers, it is difficult to see why the absence of the methyl group should confer such stability to acetal (7). At higher temperature (150°) the reaction



mixture gave ca. 15% of aldehyde mixture [(8) and (9)] and 50% of the acetal (7). We then examined the reaction of 3-furylmethanol, with the aim of synthesizing the naturally occurring terpenes perillene (10),⁹ torreyal (11), neotorreyol (12),¹⁰ and dendrolasin (13).^{10,11}

3-Furylmethanol and 1-ethoxy-2-methylbuta-1,3-diene $(100^{\circ} \text{ for } 15-24 \text{ hr.})$ yielded only the ether (14) the



n.m.r. spectrum of which showed that both cis- and transisomers were present (9:11). Pyrolysis of these at

⁹ (a) Occurring in the oil of the plant *Perilla citriodora* (H. Suzuki, J. Pharm. Soc. Japan, 1936, 56, 841); (b) also in the ant Lasius fulginosus (A. Baggini and M. Pavan, Tetrahedron Letters, 1967, 3893).

¹⁰ Occurring in Torrega nucifera oil (T. Sakai, K. Nishimura, and Y. Hirose, Bull. Chem. Soc. Japan, 1965, 38, 381).

350° gave a mixture from which the desired aldehyde (15) was isolated as the main product. A second aldehyde isolated from the reaction was not a different ring-substituted isomer of compound (9), but the monosubstituted furan (16).

Apart from the n.m.r. spectrum,² the mass spectrum of compound (16) is completely different from that of compound (9), and has its principal fragment at m/e 81, like all furans substituted with a CH₂R group.¹² The aldehydes were easily separated by chromatography on silica gel; the aldehyde (15) was reduced with lithium aluminium hydride to a mixture of the cis- and transalcohols (17a) and (17b). In order to find the best conditions for reducing either the aldehydes (15) or the alcohols (17) to perillene (10), use was again made of the 2-substituted analogues as models (3) and the corresponding alcohol (18)].



Sakai et al. reduced torreyal (11) to dendrolasin (13), with a modified Wolff-Kishner reduction.¹⁰ We found reduction of (5) by conventional Huang-Minlon techniques gave as the main, indeed almost the only product, the methylene compound (19). This reaction is known to cause rearrangement of the double-bond 13,14 and although we later were able to confirm the correctness of the Japanese work (see below), we now adopted a procedure that we had found to be not susceptible to such rearrangements, namely lithium aluminium hydride reduction of the toluene-p-sulphonate of the alcohol (without isolation of the tosylate). By this procedure, perillene (10) was obtained without difficulty from the alcohol mixture (17). Although no product was available for direct comparison, there is no doubt from the spectra and analyses that our synthetic product was pure perillene.

Since we had already shown that allyl alcohols of the type (17a) and (17b) give approximately the same proportion of products when subjected to the reaction with 1-ethoxy-2-methylbuta-1,3-diene¹ we did not separate the alcohols (17) for the next stage of the synthesis, but once again subjected the mixture to the reaction at 100° in the presence of mercuric acetate. As expected, the main product was torreyal (11).

¹¹ Occurring in the ant Lasius fulginosus (A. Quilico, F. Piozzi, and M. Pavan, Tetrahedron, 1957, 1, 177). ¹² R. Grigg, M. V. Sargent, D. H. Williams, and J. A. Knight, Tetrahedron, 1965, 21, 3441.

¹³ R. Fisher, G. Lardelli, and O. Jeger, *Helv. Chim. Acta*, 1950,
33, 1335; Swiss Pat. 282,377/October 12, 1948).
¹⁴ I. Elphimoff-Felkin and M. Verrier, *Tetrahedron Letters*,

1968, 1515.

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Chromatography on silica gel and gas chromatography of this gave a compound that had an identical mass spectrum and almost identical i.r.-spectrum with natural torreyal.¹⁰ The n.m.r.-spectrum was identical except for the presence of an additional signal at 9.98 p.p.m., characteristic of a cis-2-methyl-2-enal,¹⁵ integration implying that ca. 20% of the mixture was a *cis*-aldehyde. As with previous examples of 2-methyl-3-substituted allyl alcohols,1 no compound with a differentc onfiguration about the other double bond (at C-6 from the aldehyde group) was detected. Lithium aluminium hydride reduction gave the alcohol, neotorreyol (12) (containing cis-isomer), and treatment of the tosylate of this alcohol with lithium aluminium hydride gave pure dendrolasin (13). We repeated the distillation of torreyal semicarbazone with potassium hydroxide.10 With pellets of hydroxide (i.e. still containing water), we obtained a mixture of dendrolasin and its terminal methylene isomer (see Experimental section); it is possible that with completely dry reagents the rearrangement could be suppressed *).

That different by-products were observed in the rearrangement of the diene ethers of 2-furylmethanol (low-temperature reaction) and 3-furylmethanol (hightemperature reaction) suggests a duality of mechanism, that we can conveniently designate 'concerted' and 'biradical', depending on whether the bond-breaking and bond-making occur by simultaneous electron rearrangement or by separation and recombination of radicals. In the former case, reaction between (1) and (2) must pass through the intermediate stages (a) and (b), whilst in the latter case must give rise to radicals of the type (c), in which recombination could occur on the oxygen, C-2, or C-4, leading to (14), (16), or (15). Experiments are in progress to measure the extent of each mechanism in a related system.¹⁷



It would be interesting to speculate on the reason why 2-furylmethanol vinyl ethers can be prepared and are even distillable,⁴ while the butadienyl ethers are so thermolabile; the fact that rearrangement of the 3substituted ether requires so much more energy than the 2-substituted ethers is again not easily explained. Any reasoning involving availability of electrons in the 2- or 3-positions, such as is used in explanations of electrophilic substitution, presupposes a direction of electron movement in intermediates in Cope reactions, and must therefore be avoided. The reactions are, of course, complicated by an ensuing second step, and these factors, together with the presence of heteroatoms, make any detailed reasoning highly doubtful at this stage.

EXPERIMENTAL

M.p.s were taken in capillaries and are corrected. I.r. spectra were measured with a Perkin-Elmer type 125 spectrophotometer. U.v. spectra were obtained with an Optica type CF4 NI instrument. N.m.r. spectra were measured in carbon tetrachloride with a Varian A60 spectrometer and are quoted with respect to tetramethylsilane. Mass spectra were obtained on an Atlas CH 4 instrument, with an inlet temperature of ca. 150° and electrons of 70 ev energy; fragment ion values are given as m/e (% of main fragment). G.l.c. was carried out for analytical purposes on a Carlo Erba type GT instrument or a model 59T †; preparative g.l.c. was effected on a Carlo Erba Fractovap type P. In all cases the stationary phase was Carbowax 20M on Chromosorb W. T.l.c. was carried out on commercially available glass plates coated with silica gel (Merck Co., Darmstadt), with benzene-chloroform as solvents.

The preparation of 1-ethoxy-2-methylbuta-1,3-diene has been described.¹ 1-Ethoxy- and 1-methoxybutadiene were also made as described earlier.¹

Reaction of 2-Furylmethanol with 1-Ethoxy-2-methylbuta-1,3-diene. A mixture of furylmethanol (20 g.), 1-ethoxy-2methylbuta-1,3-diene (50 g.), mercuric acetate (6.6 g.), and anhydrous sodium acetate (2.7 g.) was heated for 18 hr. at 100° and then distilled. A fraction (21 g.), b.p. 48- $49.5^{\circ}/0.05$ mm., was chromatographed on silica gel; the following were obtained on elution with benzene. (i) A substance eluted almost immediately was converted into the main components on distillation and which was presumed to be the diene ether of furylmethanol; this was not examined further.

(ii) 2-Methyl-2-(2-methyl-3-furyl)but-3-enol (4) (0.7 g.), which was purified by g.l.c.; τ 8.59 (s, 3H, CH₃), 7.85 (s, 3H, CH₃ on furan), 4.97 (d with some further splitting, 1H, J 17.5 c./sec.), 4.73 (d with some further splitting, 1H, J 10.5 c./sec.), 3.87 (q, 1H, J 10.5 and 17.5 c./sec.), the last three signals characteristic of CH=CH₂, 3.81 (1H, furan α -H), 2.79 (1H, furan β -H), and 0.68 (s, 1H, -CHO); m/e (%): 164 (9), 135 (100), 91 (40), 81 (38), and 43 (38); only end absorption was observed in the u.v. spectrum (Found: C, 73.45; H, 7.5. C₁₀H₁₂O₂ requires C, 73.15; H, 7.35); semicarbazone, m.p. 149—149.5° (from methanol) (Found: C, 59.95; H, 6.95; N, 18.9. C₁₁H₁₅N₃O₂ requires C, 59.7; H, 6.85; N, 19.0%).

(iii) A trace of furylmethyl acetate, identical with known material.

(iv) 5-(2-Furyl)-2-methylpent-2-enal (3) (7 g.), 95% of which was judged to be the trans-isomer, from the n.m.r. signals of the aldehyde proton; τ 8·31 (s, 3H, CH₃), 7·25 (m, 4H, \cdot CH₂CH₂), 4·05, 3·78, and 2·72 [3H, furan α -H (1) and β -H (2)], 3·61br (t, 1H, \geq C=CH⁻), and 0·72 (and 0·05) [s, trans- (and cis-) -CHO], m/e 164 (4), 135 (3), 81 (100), and 53 (13) (Found: C, 73·15; H, 7·35. C₁₀H₁₂O₂ requires C, 73·15; H, 7·35%); semicarbazone, m.p. 183–184° (from methanol) (Found: C, 59·85; H, 7·0; N, 18·7. C₁₁H₁₅N₃O₂ requires C, 59·7; H, 6·85; N, 19·0); 2,4-dinitrophenylhydrazone, m.p. 137–139° (from ethanol) (Found: N, 15·7. C₁₈H₁₆N₄O₅ requires N, 16·25%).

5-(2-Furyl)-2-methylpent-2-enol. The aldehyde (3) ($3\cdot 4$ g.) was reduced with an excess of lithium aluminium hydride

¹⁶ Y. Hirose, personal communication.

^{*} The Japanese work involved the use of dry potassium hydroxide.¹⁶

⁺ Built by E. Palluy, Firmenich et Cie.

¹⁵ A. F. Thomas and M. Ozainne, Chem. Comm., 1969, 46.

¹⁷ A. F. Thomas and G. Ohloff, unpublished work.

in ether at room temperature, to give the title compound (2·3 g.), b.p. 66°/0·02 mm.; τ 8·40 (s, 3H, CH₃–C=C), 7·8 to 7·2 (m, 4H, CH₂CH₂), 6·17br (s, 2H, CH₂O), 4·64br (t, J 6·5 c./sec.), 4·1, 3·85, and 2·80 (furan protons), with a small signal at 8·28 (s) corresponding to the *cis*-alcohol (10% of the total); *m/e* 166 (3), 148 (5), 112 (8), 84 (8), 83 (9), 82 (15), 81 (100), 53 (13), and 43 (24) (Found: C, 72·05; H, 8·75. C₁₀H₁₄O₂ requires C, 72·25; H, 8·5%).

5-(2-Furyl)-2-methylpent-1-ene (19).—A mixture of 5-(2furyl)-2-methylpent-2-enal (2.5 g.) and hydrazine hydrate (3 g.) in ethylene glycol (50 ml.) was heated at reflux for 30 min. After the addition of potassium hydroxide (12 g.) in a little water, the mixture was distilled slowly for 1 hr.; the product was isolated from the distillate with pentane was distilled (b.p. $37^{\circ}/0.03$ mm.) and (0.9 g.); $\tau 8.29$ (s, 3H, $CH_3C=$), 8.4 to 7.8 (m, 4H, CH_2CH_2), 7.40 (t, J 7 c./sec., 2H, $CH_2CH_2C=C$), 5.30 (s, 2H, $C=CH_2$), 4.1, 3.85, and 2.8 (furyl H); m/e 150 (6), 94 (100), 81 (34), 69 (5), 53 (9), 41 (11); v_{max} (liq.) 3068, 1645, 1595, 1004, 921, 885, 793, and 725 cm.⁻¹ (Found: C, 80.05; H, 9.5. $C_{10}H_{14}O$ requires C, 79.95; H, 9.4%).

2-Methyl-5-(2-thienyl)pent-2-enal (5).-A mixture of 2furylmethanol (10 g.), 1-ethoxy-2-methylbuta-1,3-diene (25 g.), mercuric acetate $(3\cdot3 g.)$, and sodium acetate (1.75 g.) was heated at 100° for 18 hr. The mixture was distilled to give a fraction (12 g.), b.p. $110-130^{\circ}/0.05$ mm.; chromatography on silica gel resulted in elution of a mixture (1.1 g.) which, after rechromatographing on silica gel gave almost equal amounts of di-2-thienyl ether, identical with authentic material, and the title compound (total yield 0.15 g.), which was purified by distillation (bath temp. 160°/10 mm.); τ 8·30 (s, 3H, CH₃·C=), 7·4-6·9 (m, 4H, CH₂CH₂), 3.62 (t, J 6.5 c./sec., CH₂-CH=C), (3.35-2.85 (m, 3H, thiophen H), and 0.73 (s, 1H, CHO); m/e 180 (3), 151 (1), 122 (3), 112 (3), 97 (100), 53 (5), and 45 (8) (Found: C, 66.75; H, 6.95. C10H12OS requires C, 66.65; H, 6.7).

Reaction of 2-Furylmethanol with 1-Methoxybuta-1,3-diene. —A mixture of furylmethanol (10 g.), methoxybutadiene (25 g.), mercuric acetate (3 g.), and sodium acetate (1 g.) was heated in a sealed tube for 4 hr. at 150° and then distilled. A fraction (11.9 g.), b.p. 60—73°/10 mm., was shown by t.l.c. to contain five compounds. Chromatography in benzene on silica gel gave the following fractions: (i) trans-1-(2-furylmethoxy)buta-1,3-diene (6). The solution containing this compound was concentrated under reduced pressure (yield 0.5 g., 5%), but attempted purification by distillation or gas chromatography led to extensive rearrangement to the aldehydes described below; analyses of undistilled material: n_D^{20} 1.5199, d_4^{20} 1.0456; τ 5.38

(s, 2H, furyl-CH₂-O), 5.28 (dd, J 6.5 and 2 c./sec., 1H, H > C = C < H > H), 5.06 (dd, J 12.5 and 2 c./sec., 1H, H > C = C < H > H), 4.37 (dd, J 10.5 and 12.5 c./sec., 1H,

O-CH=CH trans; cis would appear at ca. 6.5 p.p.m.), ca. 3.85 (theor. 6 lines, partly overlapping with furan signals, CH=CH₂), 3.48 (d, J 12.5, c./sec., 1H, O-CH=CH trans), ca. 3.85, ca. 2.7 (3H, furyl H); m/e 150 (4), 91 (4), 81 (100), 53 (20), and 39 (6) (Found: C, 71.8; H, 6.65. C₉H₁₀O₂ requires C, 72.0; H, 6.7%).

* Several examples of the varying chemical shifts of such cisand trans-dienes are known, e.g. G. Ohloff, J. Seibl, and E. sz. Kovats, Annalen, 1964, 675, 83. (ii) 1-(2-Furylmethoxy)-1-methoxybut-2-ene (7).—Since this compound (yield ca. 32% by g.l.c.) decomposed on silica gel, it was purified by preparative gas chromatography and distillation (b.p. 101—102°/10 mm.); τ 8·31 (d, J 5·5 c./sec., 3H, CH₃-CH=), 6·82 (s, 3H, CH₃O-), 5·61 (s, 2H, furyl-CH₂-O), 5·18 (d, J 4 c./sec., $\stackrel{O}{O}$ CH—CH=), 4·9—4·0 (m, 2H, CH=CH), ca. 3·8, ca. 2·7 (furan H); m/e 182 (<1), 150 (1), 121 (6), 112 (39), 85 (100), 81 (95), 69 (7), 55 (22), and 53 (25) (Found: C, 66·45; H, 7·3.

 $C_{10}H_{14}O_3$ requires C, 65.9; H, 7.75%). (iii) A trace of difurfuryl ether, identical with authentic material.

(iv) 5-(1-Furyl)pent-2-enal (8) (10%). This compound was purified by preparative gas chromatography. It contained ca. 10% of an impurity [see (v) below] that was separated by g.l.c.; τ 7.6—7.0 (m, 4H, CH_2CH_2), ca. 4.05 (m, 1H, CH=), 3.5 to 3.0 (m, 1H, CH=), 3.8, 2.8 (furyl H), and 0.62 (d, J 7 c./sec., 1H, C=CH-CHO); m/e 150 (10), 94 (2), 81 (100), 53 (16), and 39 (5) (Found: C, 71.6; H, 6.85. $C_9H_{10}O_2$ requires C, 72.0; H, 6.7%); semicarbazone, m.p. 185° (from methanol) (Found: N, 20.45. $C_{10}H_{13}N_3O_2$ requires N, 20.3%).

(v) 2-(2-Methyl-3-furyl)but-2-enal (9). The compound was purified by g.l.c.; $\tau 8.05$ (d, J 7 c./sec., 3H, CH_3 -CH=), 2.11 (s, 3H, CH_3 -furyl), 6.69 (q, J 7 c./sec., 1H, =CH-CH₃), 0.59 (s, 1H, C=C-CHO), 3.85, and 2.77 (furyl H); m/e 150 (100), 135 (4), 121 (33), 109 (15), 107 (12), 103 (6), 93 (16), 91 (31), 79 (15), and 77 (51).

(vi) This was furylmethanol and g.l.c. showed that it accounted for ca. 34% of the mixture that had been chromatographed.

Reaction of 3-Furylmethanol with 1-Ethoxy-2-methylbuta-1,3-diene.—A mixture of 3-furylmethanol¹⁸ (10 g.), 1ethoxy-2-methylbuta-1,3-diene (25 g.), mercuric acetate (3.3 g.), and sodium acetate (1.4 g.) was heated at 100° for 20 hr.; the mixture was filtered and distilled to give a fraction (14.2 g.) with b.p. 65-135°/10 mm. Purified by gas chromatography, this was identified as a mixture of 45% cis- and 55% trans-1-(3-furyloxy)-2-methylbuta-1,3diene (b.p. 98°/10 mm. undecomp.); τ (selected signals) * 8.33 and 8.40 (s, 3H together, CH3 on cis- and trans- $CH=C(CH_3)-H=CH_2$, 5.40 and 5.36 (s, 2H together, furyl CH_2 -O (two isomers)), 3.89 (dd, J ca. 11 and 18 c./sec.) and 6.82 (dd, J 10.5 and 17 c./sec.), (trans- and cis-C=CH(Me).-CH₂); m/e 164 (7), 81 (100), 53 (17), and 39 (3) (Found: C, 72.6; H, 7.4. C₁₀H₁₂O₂ requires C, 73.15; H, 7·35%).

Pyrolysis of 1-(3-Furyloxy)-2-methylbuta-1,3-diene.—The ether (126 g.) was pyrolysed by passage through a glass column (46 cm. \times 2 cm. diam.) filled with glass helices and heated to 400° in a current of nitrogen. The pyrolysate was distilled, the fraction (50·2 g., 41%), b.p. 65—90°/0·3 mm.) was a mixture of cis- and trans-2-methyl-5-(3-furyl)pent-2-enal, and was used without further purification in the next stage. In order to examine the pyrolysis more carefully, it was carried out in the injection chamber of a gas chromatograph heated to 380°. Among the lighter products (ca. 43% of the total) 3-furylmethanol and unchanged ether (ca. 1:1) were identified; two other compounds were (a) 3-furylmethyl formate: τ 4·98 (s, 2H, furyl-CH₂-O), 3·6, 2·65, and 2·55 (furyl H), 2·01 (s, 1H,

¹⁸ T. Reichstein, A. Grüssner, K. Schindler, and E. Hardmeier, *Helv. Chim. Acta*, 1933, **16**, 276; E. Sherman and E. D. Amstutz, *J. Amer. Chem. Soc.*, 1950, **72**, 2195.

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O-CH=O); m/e 126 (68), 98 (51), 97 (21), 81 (100), 80 (24), 79 (26), 70 (16), 69 (25), and 53 (73); (b) 2-methyl-2-(3-furylmethyl)but-3-enal (16); τ 8.87 [s, 3H, CH₃-C (satd.)], 7.31 (2H, s, furyl-CH₂-C), 5.1 to 4.6 (m, 2H, C=CH₂), 4.17 (dd, J 10.5 and 16.5 c./sec., CH=CH₂), 3.85, 2.85, 2.75 (furyl H), and 0.27 (CHO); m/e 164 (4), 146 (5), 135 (9), 91 (12), 81 (100), and 53 (21).

The main product, 2-methyl-5-(3-furyl)pent-2-enal (15), was purified by g.l.c.; it contained (n.m.r.) 85% trans- and 15% cis-isomer; τ 8·31 (s, 3H, CH₃), 7·42 and 7·37 (4H, CH₂CH₂), 3·8, 2·8, 2·7 (furyl H), 0·72 and 0·03 (intensity ratio 83:17, s, 1H together, trans- and cis-C=C-CHO); m/e 164 (12), 149 (1), 146 (3), 136 (5), 135 (4), 107 (6), 81 (100), and 53 (19) (Found: C, 72·9; H, 7·4. C₁₀H₁₂O₂ requires C, 73·15; H, 7·35%); semicarbazone (presumably trans), m.p. 180–182° (from ethanol) (Found: C, 59·25; H, 7·1; H, 18·6. C₁₁H₁₅N₃O₂ requires C, 59·7; N, 6·85; N, 19·0%).

cis- and trans-2-Methyl-5-(3-furyl)pent-2-enol (17).--The crude aldehyde (50.2 g.) was reduced with lithium aluminium hydride (7.0 g.) in dry ether (500 ml.) at 10° . After decomposition of the complex with a little water, filtration and concentration, the alcohols were distilled, to give a mixture (43.7 g.), b.p. 75-80°/0.005 mm.), which g.l.c. showed to contain the title compounds (36% of cis- and 64% of trans-isomer); the retention times on Carbowax columns being in that order, with structures attributed on grounds of n.m.r. spectra (Found: C, 72.45; H, 8.8. C₁₀H₁₄O₂ requires C, 72.25; H, 8.5%); cis- (17a) τ 8.29 (d, J 1.0 c./sec., 3H, CH₃C=), 8.0-7.5 (m, with sharp max. at 7.67, 4H, CH2CH2), 6.08 (s, 2H, =C-CH2-O), 5.0-4.7 (m, 1H, C=CH), 3.85, 2.9, and 2.8 (furyl H); trans-(17b), 8.43 (s, 3H, CH₃C=), 7.8-7.3 (m, with sharp max. at 7.67, 4H, CH2CH2), 6.20 (s, 2H, =C-CH2-O), 4.68 (diffuse t, J 6.5 c./sec., C=CH), 3.85, 2.9, and 2.8 (furyl H); m/e (practically identical for both isomers): 166 (2), 148 (1), 137 (4), 135 (5), 95 (10), 84 (15), 83 (22), 82 (47), 81 (100), 53 (19), and 54 (59).

Perillene (10). The mixture of cis- and trans-5-(3furyl)-2-methylpent-2-enols (1 g.) was dissolved in ether containing toluene-p-sulphonyl chloride (1.2 g.); anhydrous potassium hydroxide (0.7 g.) was then added to the stirred solution at 0° during 3 hr. The mixture was stirred for a further 3 hr., during which time it was allowed to come to room temperature. After filtration and concentration (<15°), dry tetrahydrofuran (30 ml.) was added and the solution was cooled to 0°. A large excess of lithium aluminium hydride (ca. 0.3 g.) was added and the solution was allowed to come to room temperature; it was then stirred for a further 30 min. before the excess of hydride was decomposed with water. The product (0.5 g.) was isolated in pentane and was shown to contain ca. 25% of starting material and 75% perillene; the latter was purified by g.l.c. Spectral data were identical with those published, 96 m/e 150 (52), 135 (6), 94 (5), 82 (26), 81 (68), 69 (100), 53 (18), and 41 (79) (Found: C, 80.3; H, 9.35. C10H14O requires C, 79.95; H, 9.4%).

Torreyal (11). A mixture of 2-methyl-5-(3-furyl)pent-2enol (6.5 g.), 1-ethoxy-2-methylbuta-1,3-diene (20 g.), mercuric acetate (3.3 g.), and sodium acetate (1.7 g.) was heated at 100° for 18 hr. Upon distillation, material (7.5 g.) with b.p. $85-111^{\circ}/0.001$ mm. was obtained. This was chromatographed on silica gel (50 g.), the separation being followed by t.l.c. The torreyal-containing fractions were combined and, after evaporation of the solvent, the residue was distilled to give torreyal (0.8 g.), b.p. 138°/0.001 mm. For analysis, it was further purified by g.l.c., but the main bulk was used directly for the reduction step; n.m.r. identical with that reported,¹⁰ with an additional signal at $\tau 0.02$; m/e 232 (1), 217 (1), 214 (2), 201 (2), 151 (6), 93 (14), 82 (17), 81 (100), 55 (21), 53 (15), 43 (9), and 41 (10) (Found: C, 77.4; H, 8.9. C₁₅H₂₀O₂ requires C, 77.55; H, 8.7%); the *semicarbazone* m.p. and mixed m.p. 131—132° (recrystallized from ethanol and then repeatedly from pure benzene) (Found: N, 14.9. C₁₆H₂₃N₃O₂ requires N, 14.5%).

Neotorreyol * (12).—Torreyal (0.6 g.) was reduced with excess of lithium aluminium hydride in ether (5 ml.). The excess of reagent was decomposed with water and the filtered, organic solution was concentrated and the residue distilled to yield neotorreyol (0.45 g.), b.p. $163^{\circ}/0.001$ mm.; n.m.r. spectrum identical with the published one ¹⁰ with an additional signal at τ 5.99; m/e 234 (1), 219 (2), 216 (1), 203 (3), 201 (2), 135 (12), 95 (19), 93 (15), 82 (28), 81 (100), 69 (13), 55 (16), and 53 (18) (Found: C, 77.05; H, 9.4. C₁₅H₂₂O₂ requires C, 76.9; H, 9.45%).

Dendrolasin (13).-To neotorreyol (350 mg.) and toluenep-sulphonyl chloride (285 mg.) dissolved in absolute ether (15 ml.), was added powdered dry potassium hydroxide (170 mg.) at 0° during 3 hr. The mixture was stirred for a further 3 hr., then allowed to come to room temperature. After filtration and concentration below 10°, tetrahydrofuran (25 ml.) was added at 0°, followed by lithium aluminium hydride (200 mg.). The mixture was allowed to come to room temperature and then stirred for a further 30 min. before the excess of hydride was decomposed with water. The product was isolated with pentane and purified by g.l.c.; its retention time was the same as that of the natural product. The spectra (n.m.r. and i.r.) were identical with the published ones; 10 m/e 218 (4), 203 (7), 175 (10), 136 (7), 95 (6), 82 (12), 81 (65), 69 (100), 53 (12), and 41 (36) (Found: C, 82.7; H, 10.0. C₁₅H₂₂O requires C, 82.5; H, 10.15%).

Treatment of Torreyal Semicarbazone with Potassium Hydroxide.—The directions given by Hirose et al.¹⁰ were followed, but without any special precautions to dry the potassium hydroxide. The dendrolasin that was distilled from the reaction mixture was purified by g.l.c. (on the 9 mm. diam. columns used for this only a single peak was visible), and the n.m.r. spectrum of the product was that of authentic dendrolasin with other signals superimposed. In particular, integration of the singlet at τ 5.38 (C=CH₂), which is not present in the n.m.r. spectrum of dendrolasin, showed that ca. 60% of the mixture was 1-(3-furyl)-4,8nona-3,8-diene and 40% of dendrolasin (the 3,7-diene).

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* The dinitrobenzoate described in the preliminary communication is of doubtful constitution and should be disregarded.