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SYNTHESIS OF TETRAHYDRO- AND PERHYDRO-DENDROLASIN

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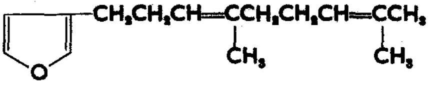
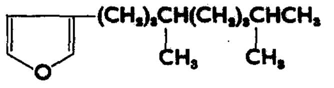
Abstract—Structure (I) of β-(4:8-dimethylnona-3:7-dienyl) furan assigned by the authors to *dendrolasin* on the basis of the chemical and spectrochemical evidence reported in a previous paper, has been confirmed by the synthesis of its hydroderivatives.

Tetrahydrodendrolasin (II) [β-(4:8-dimethylnonyl) furan] has been prepared by condensation of β-furoyl chloride with tetrahydrogeranylcadmium and subsequent Wolff-Kishner reduction of the resulting ketone (XII). *Perhydrodendrolasin* (III) [β-(4:8-dimethylnonyl) tetrahydrofuran] has been synthesised: (a) by Stobbe condensation of 4:8-dimethylnonoic aldehyde (V) with ethyl succinate, followed by reduction to 2-(4′:8′-dimethylnonyl) butandiol-1:4 (VIII) and dehydration of this last to the corresponding tetrahydrofuran derivative (III) (b) by catalytic hydrogenation of the synthetic tetrahydro-derivative (II). Synthetic tetrahydro- and perhydrodendrolasin have proved in every respect to be identical with the corresponding hydroderivatives of natural dendrolasin.

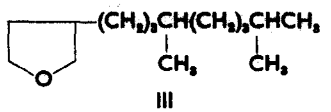
As reported in a previous paper,[1] the results of chemical investigations on *dendrolasin*, the odourous substance $C_{15}H_{22}O$ produced by the ant *Lasius* (*Dendrolasius*) *fuliginosus* Latr., had led us to assign to this product the structure of β-(4:8-*dimethylnona*-3:7-*dienyl*) *furan* (I):



I



II



III

Formula (I), which is in excellent agreement with the i.r. spectrum data of the substance and its hydroderivatives, appeared also convincing from the biogenetic point of view, since it could be derived from the head to tail linking of three isoprene units. It was however necessary to give a direct confirmation of structure (I), and this could be achieved only through the synthesis of dendrolasin or its hydroderivatives (II) and (III).

Synthesis of β-alkylfurans has been achieved in a few cases*; considering the difficulties marking the introduction of the long unsaturated isoprenoid chain contained in dendrolasin, we decided to direct our attempts first to the preparation of its hydroderivatives.

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* Only three β-alkylfurans are reported in the literature, that is: β-methyl, β-*iso*propyl and β-*iso*hexylfuran. This last (dihydroperillene) has been obtained by catalytic hydrogenation of perillene. No i.r. spectrum data of β-alkyl furans were available till now.

[1] A. Quilico, F. Piozzi, and M. Pavan *Tetrahedron* 1, 177 (1957).

Among the different routes which could be planned for the synthesis of *perhydrodendrolasin* (III), those summarised in (A) and (B) appeared most convenient,[2]*

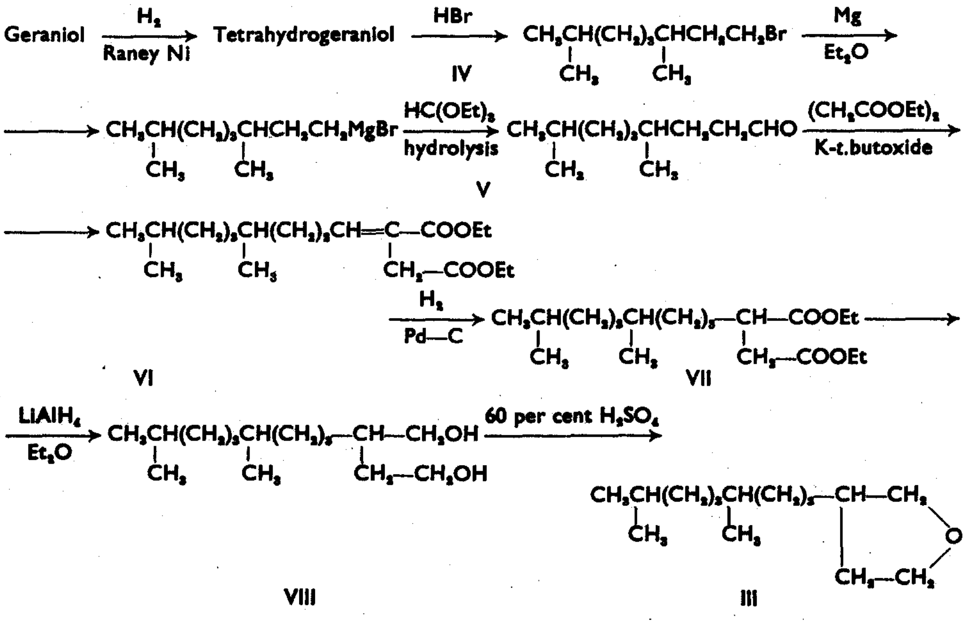
(A) Synthesis of 2-(4′:8′-dimethylnonyl)butandiol-1:4 (VIII) and subsequent cyclisation to β-(4:8-dimethylnonyl)tetrahydrofuran (III)

(B) Synthesis of β-(4:8-dimethylnonoyl)furan (XII) starting from β-furoic acid, followed by reduction to CH_2 of the CO group, and successive hydrogenation of the furan ring to tetrahydrofuran.

Tetrahydrodendrolasin (II) could be synthesised according to scheme (B) by limiting the process to the last but one stage.

Both methods (A) and (B) have been used with success. Before carrying out the syntheses with starting materials of difficult and laborious preparation such as β-furoic acid and 4:8-dimethylnonoic aldehyde required respectively by scheme (A) and (B), both processes have been tested on easily available products, in order to find the proper experimental conditions. Several models of (III), containing a simpler side chain, and some α-substituted furans (among them the α-isomer of tetrahydrodendrolasin) have been thus synthesised†.

Synthesis of *perhydrodendrolasin* (III) according to scheme (A) has been performed through the following steps:



$$\text{Geraniol} \xrightarrow[\text{Raney Ni}]{H_2} \text{Tetrahydrogeraniol} \xrightarrow{HBr} \underset{\text{IV}}{CH_3\underset{CH_3}{CH}(CH_2)_3\underset{CH_3}{CH}CH_2CH_2Br} \xrightarrow[Et_2O]{Mg}$$

$$\longrightarrow CH_3\underset{CH_3}{CH}(CH_2)_3\underset{CH_3}{CH}CH_2CH_2MgBr \xrightarrow[\text{hydrolysis}]{HC(OEt)_3} \underset{\text{V}}{CH_3\underset{CH_3}{CH}(CH_2)_3\underset{CH_3}{CH}CH_2CH_2CHO} \xrightarrow[\text{K-t.butoxide}]{(CH_2COOEt)_2}$$

$$\longrightarrow \underset{\text{VI}}{CH_3\underset{CH_3}{CH}(CH_2)_3\underset{CH_3}{CH}(CH_2)_2CH{=}\underset{CH_2-COOEt}{C}-COOEt} \xrightarrow[Pd-C]{H_2} \underset{\text{VII}}{CH_3\underset{CH_3}{CH}(CH_2)_3\underset{CH_3}{CH}(CH_2)_3-\underset{CH_2-COOEt}{CH}-COOEt} \longrightarrow$$

$$\xrightarrow[Et_2O]{LiAlH_4} \underset{\text{VIII}}{CH_3\underset{CH_3}{CH}(CH_2)_3\underset{CH_3}{CH}(CH_2)_3-\underset{CH_2-CH_2OH}{CH}-CH_2OH} \xrightarrow{60 \text{ per cent } H_2SO_4} \underset{\text{III}}{CH_3\underset{CH_3}{CH}(CH_2)_3\underset{CH_3}{CH}(CH_2)_3-\text{(tetrahydrofuran-3-yl)}}$$

Geraniol has been hydrogenated in ethanol solution over Raney nickel to tetrahydrogeraniol, and this has been transformed with HBr into tetrahydrogeranyl bromide (IV). The subsequent step which leads to 4:8-*dimethylnonoic aldehyde* (V) has

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* Both routes had been successfully applied respectively to the synthesis of α-substituted tetrahydrofurans and furans.

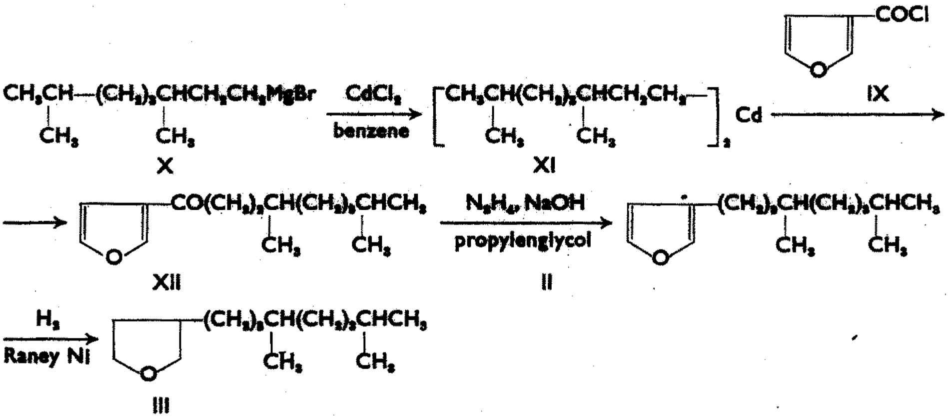
† The preparation of these compounds will be reported in a subsequent paper.

[2] W. Longinow *J. Russ. Phys. Chem. Soc.* **46**, 1084 (1914); *Ibid.* **47**, 1139 (1915); C. G. Overberger and C. W. Roberts *J. Amer. Chem. Soc.* **71**, 3618 (1949); T. Reichstein *Helv. Acta* **13**, 345 (1930); H. Gilman and N. O. Calloway *J. Amer. Chem. Soc.* **55**, 4203 (1933); N. I. Shnikin, B. V. Shemastina, and B. D. Cherkasova *J. Gen. Chem.* U.S.S.R. **8**, 674 (1938); M. Petizon and P. Baranger *C. R. Acad. Sci. Paris* **234**, 2296 (1952); *Ibid.* **236**, 499 (1953).

been achieved by condensing tetrahydrogeranylmagnesium bromide with ethyl orthoformate. The diacetal thus obtained, saponified with dilute hot sulphuric acid, gives the free aldehyde which has been purified through its bisulphite derivative. Stobbe's condensation of the aldehyde (V) with diethyl succinate afforded the diethylester (VI) of 4:8-*dimethylnonylidensuccinic acid*. The subsequent reduction of (VI) gave *diethyl 4:8-dimethylnonylsuccinate* (VII); this last, treated with lithium aluminium hydride in ether solution, produced in good yield 2-(4′:8′-*dimethylnonyl*)*butandiol*-1:4 (VIII). The final step of the synthesis, that is the dehydration of glycol (VIII) to the corresponding β-(4:8-*dimethylnonyl*)*tetrahydrofuran* (III) was carried out in 75 per cent yield by heating with 60 per cent sulphuric acid.

The product thus obtained is a colourless liquid b.p. 156°/15 mm, n_D^{20} 1·4488. It appears in any respect to be identical with *perhydrodendrolasin* prepared by catalytic hydrogenation of natural dendrolasin, as described in a previous paper.[1] A comparison of the i.r. spectra of the two products, as shown in Fig. 1, A, confirms their identity.

Synthesis of *tetrahydrodendrolasin* (II) and *perhydrodendrolasin* (III) starting from β-furoic acid, as planned in scheme (B), has been achieved as follows:



Tetrahydrogeranylcadmium (XI), prepared from tetrahydrogeranylmagnesium bromide (X) and anhydrous $CdCl_2$, has been condensed in benzene solution with β-furoyl chloride (IX). The Wolff-Kishner reduction of the thus obtained and properly purified β-(4:8-*dimethylnonoyl*)*furan* (XII) afforded in a fairly good yield β-(4:8-*dimethylnonyl*)*furan* (II). Synthetic tetrahydrodendrolasin (II) is a colourless liquid b.p. 90–91°/0·6 mm, n_D^{20} 1·4571 which turns slowly to brown on exposure to air and light. It gives a pine shaving test and a colour reaction with vanillin which are very similar to those of natural dendrolasin. Its physical and chemical characteristics demonstrate that it is identical with the tetrahydroderivative obtained by hydrogenation of dendrolasin over Pd—C—$BaSO_4$ under controlled conditions, as previously reported. The i.r. spectra shown in Fig. 1, D, also confirm the identity of the two products.

Hydrogenation of (II) in the presence of Raney nickel yielded a β-(4:8-dimethylnonyl)tetrahydrofuran (III), b.p. 120°/1·8 mm, n_D^{20} 1·4481, which proved to be identical with the product synthesised according to scheme (A), and with perhydrodendrolasin from natural source, as shown by the i.r. spectra reported in Fig. 1, B.

Although the synthesis of perhydrodendrolasin according to scheme (B) might appear more simple and direct than that achieved following the alternative route (A), it has proved to be in practice rather toilsome, because of the intervention of secondary reactions which lead to undesired by-products very difficult to eliminate. Such are: (a) *tetrahydrogeranyl β-furoate*, which always is formed in conjunction with ketone (XII) in the reaction between tetrahydrogeranylcadmium and β-furoyl chloride, even when pure tetrahydrogeranyl bromide completely free from the corresponding alcohol had been employed, and (b) 2:6:11:15-*tetramethylhexadecane* (crocetane), which is

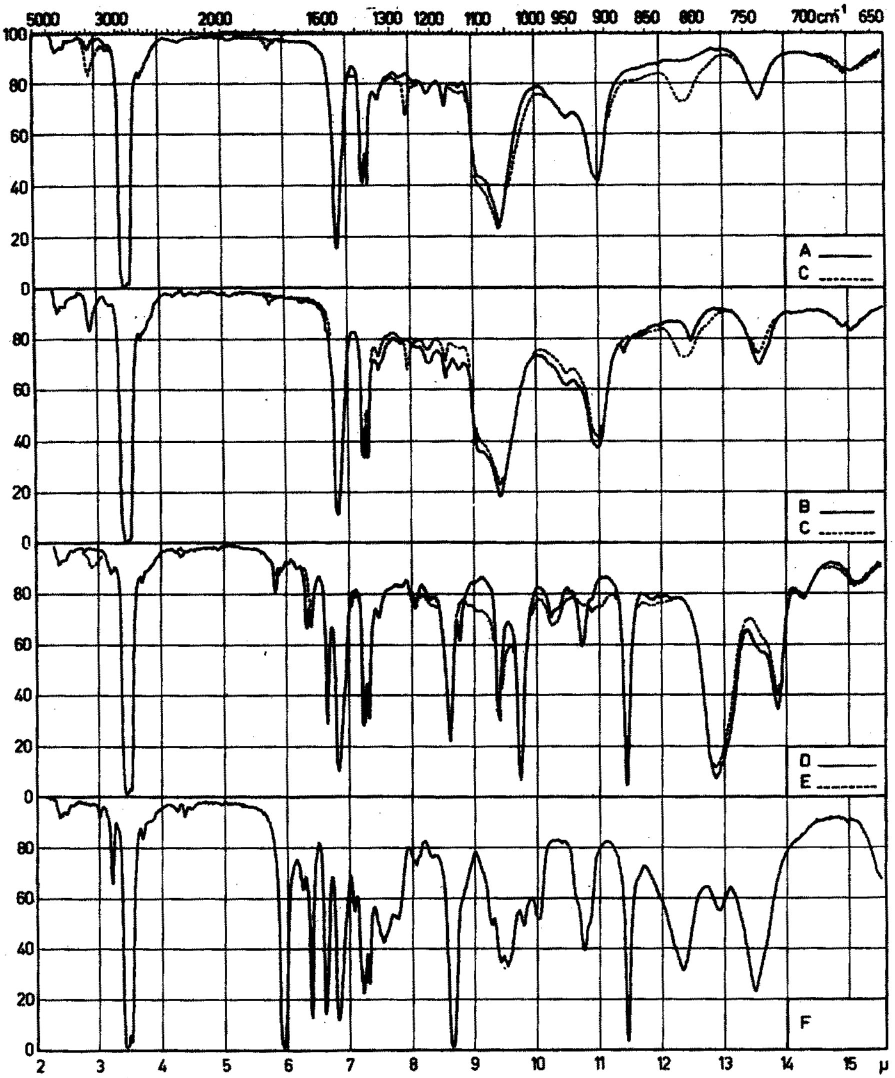


FIG. 1. Infra-red spectra

A synthetic β-(4:8-dimethylnonyl)tetrahydrofuran, via glycol, liquid 0·023 mm
B synthetic β-(4:8-dimethylnonyl)tetrahydrofuran, via β-furoic acid, liquid 0·0264 mm
C Perhydrodendrolasin, liquid 0·022 mm
D synthetic β-(4:8-dimethylnonyl)furan, liquid 0·0264 mm
E Tetrahydrodendrolasin, liquid 0·0263 mm
F β-(4:8-dimethylnonoyl)furan, liquid 0·0247 mm

formed in the action of magnesium on the bromide. i.r. spectrum have proved very helpful in this work for testing the purity of the reagents and for the identification of the secondary products formed in the different stages of the synthesis.

The above described syntheses of tetrahydro- and perhydro-dendrolasin confirm that the structure we had assigned to dendrolasin on the basis of chemical and spectrochemical evidences is correct.

EXPERIMENTAL

Preparation and purification of tetrahydrogeranyl bromide. Commercial geraniol was carefully fractionated at ordinary pressure, and the 225–230° fraction submitted to catalytic hydrogenation in ethanol solution at 120° and 50–80 atm pressure over Raney nickel W5. The product thus obtained gave on fractionation at reduced pressure pure tetrahydrogeraniol with b.p. 114–115°/17 mm, and n_D^{20} 1·4407, in agreement with the data recorded in the literature.[3] Yield 80 per cent.

A mixture of 100 g of tetrahydrogeraniol and 200 ml HBr *d* 1·48 was refluxed for 6 hr under vigorous mechanical stirring. The oily layer was washed with Na_2CO_3 solution, dried (Na_2SO_4), and then distilled *in vacuo*. The resulting tetrahydrogeranyl bromide, obtained in 75 per cent yield, boiled at 107°/18 mm; $n_D^{20\cdot5}$ 1·4528. Although its physical constants were in agreement with those assigned by literature to the pure bromide,[4] the i.r. spectrum of the product thus obtained indicated that about 5–8 per cent of the unchanged alcohol was still present. This was eliminated by treating the bromide with twice the amount of 4-nitrobenzoyl chloride required for complete esterification of the free alcohol, and the equivalent quantity of anhydrous pyridin. The mixture was heated for about 30 min, then the solid products were discarded and the liquid was fractionated twice at reduced pressure. Pure tetrahydrogeranyl bromide free from tetrahydrogeraniol (no OH bands in its i.r. spectrum) has the following physical constants: b.p. 75–76°/1 mm; n_D^{20} 1·4537.

β-Furoyl chloride was prepared by refluxing β-furoic acid with thionyl chloride in benzene solution, as reported in the literature.[5] The product we used boiled at 78–80°/55 mm and melted at 27°.

Preparation of 4:8-*dimethylnonoic aldehyde.* This compound has already been reported in the literature.[6] More convenient, for preparative purposes, is the procedure we have elaborated as follows. In a dry 1 l. four-necked flask, equipped with a Hershberg stirrer,[7] a reflux condenser, a dropping funnel and a nitrogen inlet tube, were introduced 6·1 g (0·254 g atoms) of magnesium turnings and 60 ml of anhydrous ether. About the tenth part of a solution of 56 ml (0·254 mole) of pure tetrahydrogeranyl bromide in 125 ml of ether was then added through the funnel. The reaction was initiated by the addition of a few crystals of iodine and the remainder of the bromide introduced over a period of about 1½ hr under continual stirring. The reaction mixture was then refluxed on the water-bath for 1 hr and 33·15 g (0·233 mole) of freshly distilled ethyl orthoformate were added dropwise under constant stirring. After the addition of the orthoformate, the reaction was completed by refluxing on the water-bath for 4 hr. The reaction mixture was then cooled and cautiously decomposed

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[3] S. Natelson, S. Gottfried, and S. Kornblau *J. Amer. Chem. Soc.* **64**, 1484 (1942).

[4] J. v. Braun and W. Kaiser *Ber. Dtsch. Chem. Ges.* **56**, 2272 (1923).

[5] H. Gilman and R. R. Burtner *J. Amer. Chem. Soc.* **55**, 2905 (1933).

[6] J. v. Braun and W. Kaiser *loc. cit.*; F. G. Fisher and K. Loewenberg *Liebigs Ann.* **475**, 201 (1929); I. Heilbron and A. Thompson *Soc.* 892, (1929).

[7] *Organic Syntheses* Coll. Vol. 2, p. 117.

with ice and dilute HCl. The organic layer thus separated, dried (Na_2SO_4), left after removal of the solvent the diethylacetal of 4:8-dimethylnonoic aldehyde. The hydrolysis of this last was carried out by refluxing for 1 hr with dilute H_2SO_4, taking up into ether the aldehyde set free. The crude aldehyde left after elimination of the solvent had a b.p. 84–87°/2 mm, and contained traces of halogenated products; it was therefore purified through its bisulphite derivative. For this purpose 33·5 g of aldehyde were added to the clear solution obtained by mixing 40 ml of a saturated $NaHSO_3$ solution with 40 ml of methanol, and the mixture was shaken for 6 hr in a well stoppered bottle. The white crystalline precipitate was collected, washed with methanol and ether, and then decomposed with a suspension of 10 g of $NaHCO_3$ in 80 ml of water. The aldehyde was isolated from the mixture by steam distillation, followed by extraction with ether and fractionation *in vacuo* (in the presence of trace of hydroquinone) of the oily residue left after removal of the solvent. The pure 4:8-dimethylnonoic aldehyde thus obtained weighed 7·6 g (17·5 per cent yield). It is a colourless liquid endowed with a peculiar smell, soluble in most of organic solvents. B.p. 75–76°/0·8 mm, n_D^{20} 1·4301.

Synthesis of Perhydrodendrolasin According to Scheme A

Condensation of 4:8-*dimethylnonoic aldehyde* (*V*) *with diethyl succinate : diethyl ester of* 4:8-*dimethylnonylidensuccinic acid* (*VI*).[8] To 250 ml of anhydrous *tert*-butanol contained in a ½ l. flask fitted with a reflux condenser, a dropping funnel and a nitrogen inlet tube, 8·7 g of metallic potassium were added, maintaining a continuous slow stream of nitrogen. A mixture of 44 g of diethyl succinate and 34·4 g of 4:8-dimethylnonoic aldehyde was then added to the boiling potassium-alkoxide solution, and the whole was refluxed for 24 hr in nitrogen atmosphere. After removal of the greatest part of the *tert*-butyl alcohol by distillation at reduced pressure, the reaction mixture was made slightly acidic with dilute HCl, and the remainder of the solvent removed by steam distillation. The mixture was then extracted with ether, and the extract repeatedly washed with 10 per cent Na_2CO_3 solution; the organic layer, containing some diethyl succinate was discarded. The aqueous alkaline layer, acidified with HCl and extracted with ether gave, after removal of the solvent, a brownish oil which was dissolved in ten times its volume of absolute ethanol. This solution was saturated with dry gaseous HCl, and kept at room temperature for 24 hr. After removing the HCl and the ethanol at reduced pressure, the residue was poured into ice water and extracted with ether. The ether layer, washed with Na_2CO_3 and dried (Na_2SO_4), gave a residue which was fractionated *in vacuo*. At 160°/2·5 mm diethyl succinate was recovered then, at 171–173°/2·5 mm, diethyl dimethylnonylidensuccinate distilled as a viscous oil n_D^{20} 1·4536. Yield 24 per cent (Found: C, 69·85; H, 10·54. Calc. for $C_{19}H_{34}O_4$: C, 69·90; H, 10·50 per cent).

Catalytic hydrogenation of diethyl dimethylnonylidensuccinate: diethyl ester of 4:8-*dimethylnonylsuccinic acid* (VII). 22 g of the above described diethylester, dissolved in 100 ml of ethanol, were shaken with hydrogen at room temperature and at 3 atm pressure in the presence of 0·2 g of Pd—C. The H_2 absorption was completed in 3–4 hr. After filtration of the catalyst and removal of the solvent, the residue was distilled at reduced pressure. Diethyl 4:8-dimethylnonylsuccinate is a colourless oil

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[8] G. C. Overberger and C. W. Roberts *loc. cit.*

b.p. 175–176°/4 mm with n_D^{20} 1·4404. Yield 80 per cent. (Found: C, 69·29; H, 10·73. Calc. for $C_{19}H_{36}O_4$: C, 69·47; H, 11·05 per cent.)

Reduction of diethyl dimethylnonylsuccinate with lithium aluminium hydride; 2-(4′:8′:-dimethylnonyl)butandiol-1:4 (VIII). A solution of 16·7 g of the ester in 200 ml of dry ether was refluxed with 3·8 g of $LiAlH_4$ at the water-bath for a period of 6 hr. The unaffected hydride was then decomposed with moist ether and water. The organic layer, dried (Na_2SO_4) and distilled, gave a residue which was fractionated at reduced pressure. At 159–160°/0·12 mm the glycol distilled as a viscous liquid with n_D^{20} 1·4588. Yield 10 g (about 80 per cent of the theoretical amount).

Dehydration of dimethylnonylbutandiol to β-(4:8-*dimethylnonyl)tetrahydrofuran* (*synthetic perhydrodendrolasin*) (III). The procedure described by Longinow[9] for the conversion of 1:4-glycols into the corresponding tetrahydrofurans has been employed. A mixture of 8·9 g of dimethylnonylbutandiol and 20 ml of 60 per cent (by weight) sulphuric acid was heated in a 50 ml distillation flask under reduced pressure (200 mm); a colourless emulsion was formed which gradually turned brown. The temperature was then allowed to rise to the boiling point of the mixture, and held at this point until 10 ml of distillate (which separated into two layers) were collected. The dark reaction mixture left in the distillation flask was diluted with water, made slightly alkaline and then extracted with ether. The solvent was removed and the residue steam distilled. The aqueous distillate thus obtained, combined with the portion collected during the first phase of the reaction, was again taken up into ether. Distillation of the ether solution, previously washed with Na_2CO_3, gave an oily residue which was fractionated at reduced pressure. At 156°/15 mm the β-dimethylnonyltetrahydrofuran distilled as a colourless liquid of faint odour, n_D^{20} 1·4488. Yield 6 g (about 75 per cent) (Found: C, 79·26; H, 12·98. Calc. for $C_{15}H_{30}O$: C, 79·57; H, 13·36 per cent). The i.r. spectrum of the thus prepared perhydro-dendrolasin is given in Fig. 1, A. It is practically identical with that of the product prepared by hydrogenation of dendrolasin.

Synthesis of tetrahydrodendrolasin and perhydrodendrolasin according to scheme B.

Synthesis of β-(4:8-*dimethylnonoyl)furan* (XII).[10] A solution of tetrahydrogeranylmagnesium bromide was prepared as described (p. 190), starting from 56 ml (0·254 mole) of pure tetrahydrogeranyl bromide, 6·1 g (0·254 g atom) of Mg turnings and 125 ml of anhydrous ether. Titration with N/10 H_2SO_4 and NaOH indicated that the Grignard reagent had been formed in a 86·5 per cent yield. To the cool, clear solution of the Grignard 23·6 g (0·127 mole) of recently melted anhydrous cadmium chloride were added over a period of 5–10 min. After all the $CdCl_2$ had been introduced, the mixture was stirred and heated under reflux until the Gilman test for unchanged Grignard reagent was negative (about 20 min were required). Ether was then rapidly distilled from the reaction mixture until a semisolid residue was left; at this point 80 ml of pure dry benzene were introduced, and the distillation was continued until 60 ml of the solvent were collected. An additional 70 ml portion of benzene was then added and, with continual stirring, a solution of 27 g (0·207 mole) of β-furoyl chloride in 60 ml of benzene was dropwise added at room temperature. After refluxing for about 1 hr, the reaction mixture was cooled and decomposed with ice and dilute sulphuric acid. The benzene layer was separated and the aqueous phase extracted with ether.

[9] *loc. cit.*

[10] D. A. Shirley *Org. React.* VIII 28 (1954).

The combined organic extracts, washed with $NaHCO_3$ solution and dried (Na_2SO_4), were evaporated. The oily, reddish coloured residue, fractionated at reduced pressure gave a small quantity of unchanged furoyl chloride and 37·3 g of crude ketone b.p. 150–160°/8–9 mm. Yield 76.5 per cent.

The product thus obtained contained some *tetrahydrogeranyl β-furoate* and some *crocetane* (2,6:11:15-tetramethylhexadecane) which could not be removed by distillation. The i.r. spectrum of an apparently pure specimen with b.p. 127·5°/0·5 mm and n_D^{20} 1·4631 prepared by repeated fractionation of the crude ketone, still showed the bands of the ester. To eliminate this last, the raw ketone was refluxed for 2 hr with 7 g of KOH in 100 ml of methanol. After distillation of the methanol, the residue was treated with water and the oil taken up into ether. Fractionation under reduced pressure of the oil recovered from the ether solution gave 5·7 g of tetrahydrogeraniol b.p. 75–85°/1 mm, $n_D^{20·5}$ 1·4437, and 27·2 g of a fraction b.p. 120–130°/1 mm with $n_D^{20·5}$ 1·4660. Some β-furoic acid (3·1 g) m.p. 121–122° was recovered from the aqueous alkaline phase by treatment with sulphuric acid. The high boiling fraction redistilled twice yielded 21·3 g of a colourless oil b.p. 140°/2·4 mm, $n_D^{20·5}$ 1·4667. The analysis and the i.r. spectrum indicated that this product contained about 25 per cent of crocetane.

The pure ketone was isolated from this mixture by converting it into the corresponding *phenylsemicarbazone*. 4·3 g of the product b.p. 140°/2·4 mm, dissolved in methanol and treated with 3·4 g of phenylsemicarbazide chloride and 1·65 g of $NaHCO_3$ gave, after 24 hr standing, 2·8 g of crystalline phenylsemicarbazone. Purified by recrystallisation from methanol it formed thin needles m.p. 125° (Found: N, 11·12 11·20. Calc. for $C_{22}H_{31}O_2N_3$: N, 11·37 per cent).

Pure dimethylnonoylfuran, set free from its phenylsemicarbazone by hydrolysis with boiling dilute H_2SO_4, is a colourless oil b.p. 115–116°/0·05 mm, n_D^{20} 1·4747 (Found: C, 76·07; H, 10·08. Calc. for $C_{15}H_{24}O_2$: C, 76·22; H, 10·24 per cent). It gives the vanillin reaction (brown-red) and the pine shaving reaction. Its i.r. spectrum is given in Fig. 1, F. Besides the strong CO band at 1685 cm^{-1} and the *iso*propyl group bands at 1384 and 1367 cm^{-1}, the following bands assignable to the furan system are present: 1565 and 1512 cm^{-1} (conjugated furan); 1158 873 and 741 cm^{-1} (β-substituted furan).

Dimethylnonoylfuran 2:4-*dinitrophenylhydrazone* crystallises from glacial acetic acid in orange needles m.p. 98–99° (Found: N, 13·52; Calc. for $C_{21}H_{28}O_5N_4$: N, 13·45 per cent). Both the *p*-nitrophenylhydrazone and semicarbazone were oils at ordinary temperature.

Wolff-Kishner reduction of dimethylnonylfuran: β-(4:8-*dimethylnonyl*)*furan* (*synthetic tetrahydrodendrolasin*) (II).[11] A mixture of 15 g of the ketone (purified through its phenylsemicarbazone as described) 8·6 g of NaOH, 9·5 ml of hydrazine hydrate and 130 ml of propylene glycol, was refluxed for 1 hr in nitrogen atmosphere (temperature of the liquid 146°). A portion of the liquid was then distilled until the b.p. of the reaction mixture attained 180°. After two additional hours of refluxing the mixture was poured into an excess of dilute sulphuric acid, and the oily product thus separated was extracted with ether. The portion which distilled between 146° and 180° was submitted to the same treatment. The combined extracts were washed with dilute H_2SO_4, then with water, and finally dried (Na_2SO_4). By distilling the ether solution an

[11] Huang-Minlon *J. Amer. Chem. Soc.* **68**, 2487 (1946).

oily residue was obtained which, on distillation *in vacuo*, gave 8 g of crude dimethylnonylfuran b.p. 97–102°/1·2 mm. This was purified by careful twice repeated fractionation at reduced pressure. Pure dimethylnonylfuran is a colourless oil b.p. 90–91°/0·6 mm, n_D^{20} 1·4571, which slowly turns brown on exposure to air and light (Found: C, 81·03; H, 12·34. Calc. for $C_{15}H_{26}O$; C, 81·02; H, 11·79 per cent). With vanillin in ethanol-HCl solution it gives a fine fuchsia-red colour which turns brown on heating; the pine shaving reaction is the same as that of dendrolasin (dirty blue-green).

The i.r. spectrum, reported in Fig. 1, D, is practically identical with that of the tetrahydroderivative obtained by catalytic hydrogenation of dendrolasin (Fig. 1, E).

Hydrogenation of dimethylnonylfuran with Raney nickel; β-(4:8-dimethylnonyl) tetrahydrofuran (III) (Synthetic perhydrodendrolasin). A solution of 1·85 g of synthetic tetrahydrodendrolasin in 100 ml of 95 per cent ethanol was shaken with hydrogen at room temperature and at ordinary pressure, in the presence of 2 g of Raney nickel W 5. The absorption ceased when 402 ml of H_2 (at 17° and 750 mm) had been fixed (calc. for two double bonds: 399 ml). After removal of the catalyst and the solvent, the liquid residue was distilled at reduced pressure. It yielded a colourless oil b.p. 120°/1·8 mm, n_D^{20} 1·4481. The i.r. spectrum, given in Fig. 1, B, is identical with that of perhydrodendrolasin from natural source or synthesised according to scheme A.

The authors are indebted to Dr. F. Canal of the Farmitalia Research Laboratory for some of the C,H determinations, and to Dr. E. Mantica for his assistance in the interpretation of the i.r. spectra.