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THE STRUCTURE OF INCENSOLE

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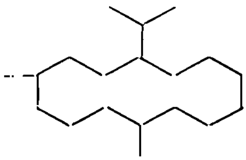
Abstract—A new diterpene alcohol, incensole (I) isolated from frankincense is related to cembrane. Chemical and physico-chemical data support the structure 12-isopropyl-1,5,9-trimethyl-1,12-oxido-5,9-cyclotetradecadien-2-ol.

Although the acidic fraction of frankincense (produced by *Boswellia carteri*) and the triterpenic acids have been thoroughly investigated,[1] very little attention has been paid to the neutral components of this resin, of which only some volatile compounds[2] have been identified.

In the course of an investigation on the neutral and unsaponificable fraction of the resin, we were able to isolate a new macrocyclic diterpene, which has the skeleton of cembrane



cembrane

This compound, incensole (I), is a diterpene similar in structure to a group recently isolated from tobacco[3] and from the resin produced by some varieties of pine trees.[4]

Incensole (I) isolated after several chromatographic separations is a low-melting solid, not crystallizable from the usual solvents. However, this material, homogeneous on TLC was a single compound, yielding only one ketone (incensone II: see later) on chromic oxidation.

Incensole (I), purified by high vacuum distillation, shows $[\alpha]_D = -77{\cdot}5°$. The molecular formula, $C_{20}H_{34}O_2$, is in accordance with its composition and the mol. wt. of the corresponding ketone II. The UV does not show absorption above 210 mμ. IR spectrum of I shows an OH band (3620 cm^{-1}), no CO absorption and an intense band at 1050 cm^{-1}, which can be attributed to an ethereal bridge.[5] The NMR spectrum

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* In alphabetical order.

[1] J. Simonsen and W. C. Ross, *The Terpenes* Vol. V; pp. 68 and 167. The University Press, Cambridge (1957); S. Corsano e G. Picconi, *Ann. Chim., Italy* **52**, 802 (1962); S. Corsano e C. Iavarone, *Gazz. Chim. Ital.* **94**, 328 (1964).

[2] E. Gildenmeister and Fr. Hofman, *Die Ätherischen Öle* Vol. V; p. 653. Akademic Press, Berlin (1959).

[3] D. L. Roberts and R. L. Rowland, *J. Org. Chem.* **27**, 3989 (1962); R. L. Rowland and D. L. Roberts, *Ibid.* **28**, 1165 (1963); R. L. Rowland, A. Rodgman, J. N. Schumacher, D. L. Roberts, L. C. Cook and W. F. Walker Jr., *Ibid.* **29**, 16 (1964).

[4] W. G. Dauben, W. E. Thiessen and P. R. Resnick, *J. Org. Chem.* **30**, 1693 (1965).

[5] As it will be shown later, this cyclic ether is five membered. Such cyclic ethers show the asymmetrical C—O—C stretching vibration between 1100 and 1075 cm^{-1}. The lower frequency observed in this case can be attributed to the ring strain; for example, trimethylene oxide absorbs between 980 and 971 cm^{-1} (See C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy* p.190. Academic Press, New York (1963)).

of incensole (Fig. 1) indicates the presence of two olefinic protons (broad signal between 4·85 and 5·20 δ) and of a proton which belongs to a secondary alcoholic function (doublet J = 10 c/s centered at 3·18 δ). Three Me groups also appear: two of them are fixed on a double bond (unsharp signals at 1·48 and 1·61 δ), the third appears fixed on a carbon which carries an oxygen atom (sharp peak at 1·02 δ). An unsharp doublet (6H; J = 6·5 c/s) centered at 0·90 δ agrees with the presence of an isopropyl group. In benzene solution this doublet is resolved into four lines, centered at 0·90 δ approximately: this pattern is typical for an isopropyl group, which has its two methyls in different magnetic environments.[6]

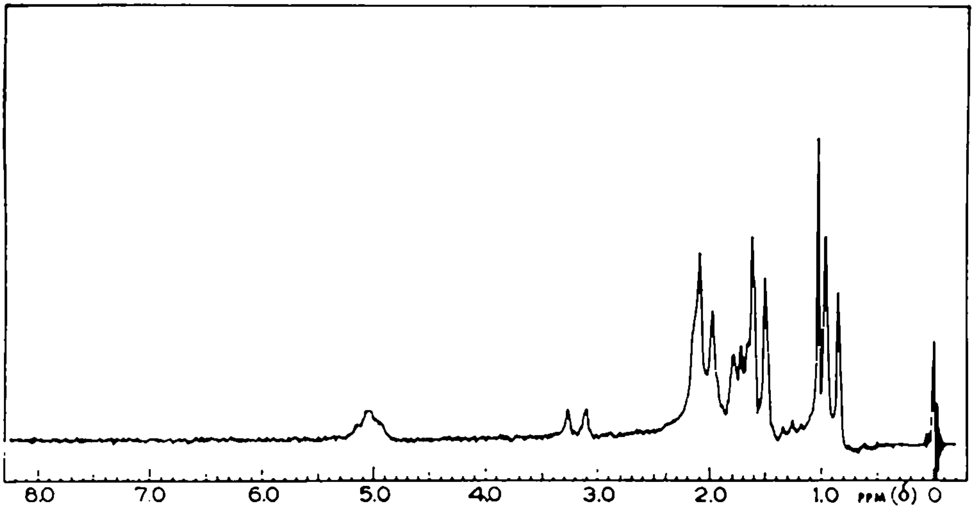

FIG. 1. NMR spectrum of incensole (I) in CCl_4 at 60 Mc.

Chromic oxidation in pyridine of incensole (I) leads to incensone (II), $C_{20}H_{32}O_2$, m.p. 42–44° and $[\alpha]_D = -20°$ which gives a 2,4-dinitrophenylhydrazone, m.p. 148–149°.

Since incensone (II) is reconverted into incensole (I) and into its epimer[7] m.p. 79–81° $[\alpha]_D = -19·2°$ by reduction with $NaBH_4$ in methanol, it is possible to exclude other modifications which may have occurred during oxidation.

The UV spectrum of II shows a max at 295 mμ (ε = 54); therefore there is no conjugation between the CO and the double bonds. The IR shows CO absorption at 1720 cm^{-1},[8] and since there is no OH absorption, the second oxygen atom must be ethereal. In comparing the NMR spectrum of II with the spectrum of I, the most relevant modification is the downfield shift of the signal due to the $\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$ group (1·02 in compound I and 1·27 in compound II). Therefore, this Me must be in α-position to the CO group.

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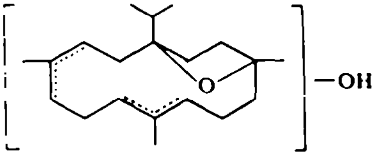
[6] Also in the case of tobacco diterpenes (see footnote 3) and of cembrene (see footnote 4) the signal of i-propyl group is split in four lines.

[7] This epimer is well distinguishable from incensole (I) by TLC. Therefore, compound I isolated from the resin cannot be contaminated by this epimer.

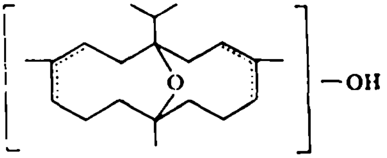
[8] An oxygen atom in α-position could account for this high value of the CO stretching frequency (see S. S. Stradling and D. S. Tarbell, *J. Org. Chem.* **29**, 1170 (1964)).

Incensole (I) absorbs two molecules of hydrogen over PtO_2 in acetic acid and gives a crystalline tetrahydroderivative (III), $C_{20}H_{38}O_2$. The latter, although behaving like an homogeneous material on TLC, has no sharp m.p.; no doubt due to the formation of a stereoisomeric mixture during hydrogenation.

The data presented support the presence of one secondary OH function, one ethereal function, and two double bonds; therefore incensole (I), $C_{20}H_{34}O_2$, must have a monocyclic C-skeleton. Since it has three Me groups and one isopropyl group, it is reasonable to correlate it with cembrane. On the other hand, the ethereal function must be ditertiary, because of the presence of only one signal attributable to hydrogens in α-position to oxygen atoms; in addition, one point of attachment of the ethereal bridge must be a carbon which carries a Me group. Consequently, the following structures, both of which are in close agreement with the spectroscopic data may be considered.



A



B

As permanganate-periodate oxidation[9] of incensole (I) yields a mixture in which methyl laevulinate (IV) was detected by gas chromatography, structure B must be excluded.

The reciprocal arrangement of the two double bonds and of the OH was determined in the following way. Careful permanganate oxidation followed by treatment of the acidic fraction with diazomethane yielded in addition to the laevulinic ester, a diketoester (V), $C_{16}H_{26}O_5$, as a liquid, b.p. 136°/0·05.

NMR spectrum of V shows the signal due to the isopropyl group (0·92 and 0·97 δ; doublets) and a sharp signal (3H) at 1·27 δ, in the same position as the signal due to $CH_3—\overset{|}{\underset{|}{C}}—O$ group in the NMR of incensone (II): therefore during the reaction, the OH group of incensole (I) is oxidized to a CO group. The diketoester (V) is a methylketone (sharp peak at 2·12 δ; positive Lieben test) and must be also a 1,4-diketone, since after treatment with NH_3 and $AcONH_4$-AcOH[10] it gives a positive pyrrole test.

These oxidation reactions, bearing in mind the indefinite structure A, clearly demonstrate the presence of the partial structure VI.[11]

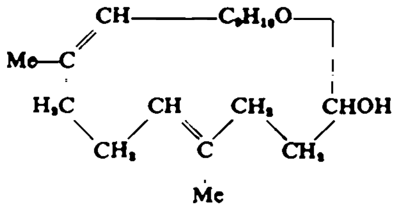
Clarification of the residual part of the molecule and the structure of incensole (I) were achieved by treatment of tetrahydroincensole (III) with acids.

While incensole (I), on treatment with acid, affords a very complex mixture (possibly due to transanular reactions), tetrahydroincensole (III) gives a mixture, from which we were able to isolate an appreciable amount of a crystalline ketone (VII),

[9] R. U. Lemieux and E. von Rudloff, *Canad. J. Chem.* 33, 1701 (1955).

[10] According to the method used by R. A. Nicolaus and L. Mangoni, *Gazz. Chim. Ital.* 86, 358 (1956).

[11] The position of the OH group in the partial structure VI is also supported by IR spectrum of incensone (II). The carbonyl group in this compound (C=O band at 1720 cm⁻¹) must be outside of the tetrahydrofuran ring, because tetrahydrofuranones absorb at 1760 cm⁻¹ (J. H. Sperna Weiland, H. Dijkstra and A. B. Pik, *Rec. Trav. Chim.* 82, 651 (1963)).



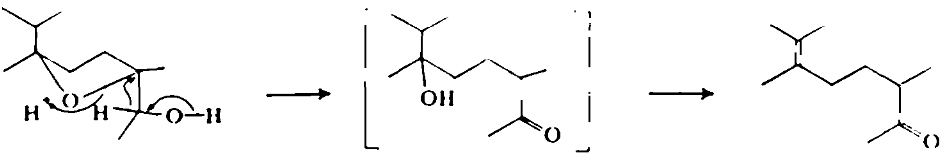
VI

$C_{20}H_{32}O$ (IR, CO band at 1710 cm^{-1}) by means of preparative gas chromatography. As derived from III, this ketone is a mixture of stereoisomers, and does not show a sharp m.p.

The NMR spectrum of VII shows the signal due to an isopropylidene group ($\delta = 1{\cdot}60$): and, therefore, the second point of attachment of ethereal bridge must be on the carbon which carries the isopropyl group.

Moreover, compound VII is an α-methyl-ketone since the spectrum shows the split signal of a Me at 1·05 δ (J = 6·5 c/s); the coupling between the α-methyl and α-hydrogen was also confirmed by double resonance experiments.[12]

As a CO group may be formed from a OH group by 1,2 hydride shift, the reaction of III with acids and the formation of a less strained system, may be represented as follows:



This interesting transformation, which is comparable to a pinacolic rearrangement,[13] clearly shows that the two atoms of oxygen are placed in 1,2 positions.

Finally, we were able to show that incensole (I) possesses the cembrane skeleton. Clemmensen reduction of VII yields a hydrocarbon[14] which is identical in its gas chromatographic behaviour and in its mass spectrum with a sample of synthetic cembrane.[15]

Having clarified the structure of incensole (I), the constitution and reactions of the compounds, described so far, are outlined on facing page.

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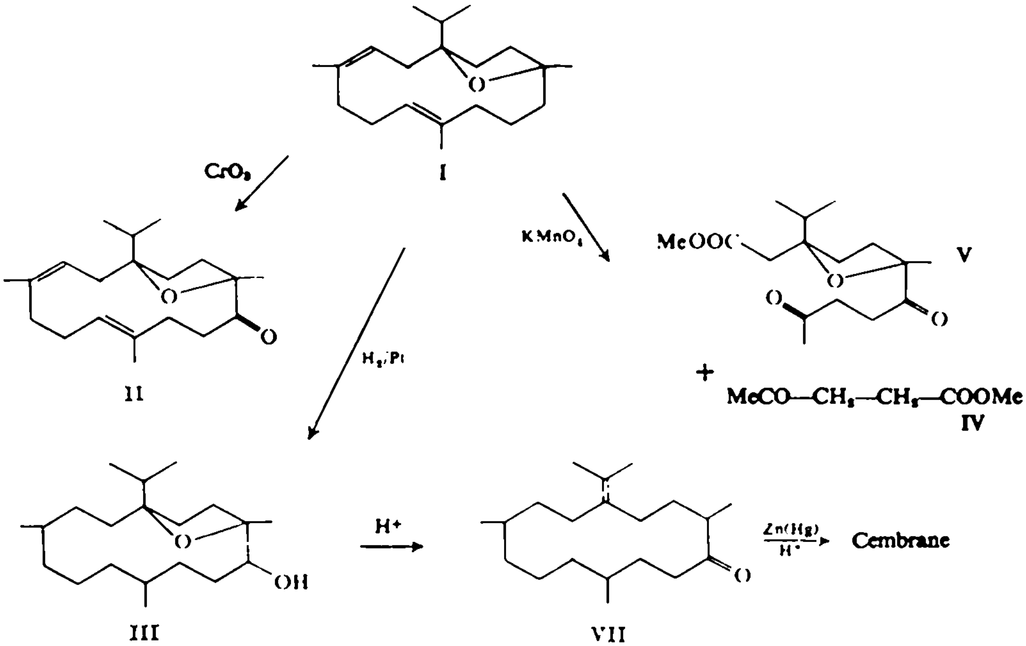
[12] The doublet centered at 1·05 tends to become a singlet by irradiation at 2·30 δ, which is the position of the signal due to the hydrogen atom in α to the carbonyl group. The incomplete decoupling is due to the large width of the hydrogen signal.

[13] P. de Mayo, *Molecular Rearrangements* Vol. I; p. 16. Interscience, New York (1963).

[14] Double bonds are often reduced during this reaction. See E. L. Martin: The Clemmensen reduction in *Organic Reactions* Vol. I; p. 161. Wiley, New York (1942).

[15] I. D. Entwistle and R. A. W. Johnstone, *Chem. Comm.* 136 (1966). The comparison of mass spectra appears the best way to compare the two cembranes which are both stereoisomeric mixtures. It is well known that different *isomers* give clearly distinguishable mass spectra, while different stereoisomers do not show very often appreciable differences in their cracking patterns. [See K. Biemann, *Mass Spectrometry* p. 144. McGraw-Hill, New York (1962).] Accordingly, Entwistle and Johnstone found that synthetic cembrane—a mixture of stereoisomers—has the same mass spectrum of the cembrane, obtained from a natural source, which is also a stereoisomeric mixture.



We should like to point out that frankincense provides an interesting example of rare co-occurrence of di- and triterpenes.[16]

It is well known that the two families of terpenes are produced in two different biogenethic pathways and it is, therefore, unusual to find both in the same source.

EXPERIMENTAL

The UV and IR spectra were recorded with a Perkin-Elmer 137 UV and a Perkin-Elmer Infracord 137, respectively.

The NMR spectra were determined in CCl_4 soln with a Varian A-60. Chemical shifts are quoted in δ-values downfield from TMS as internal standard. M.ps were taken on a Kofler hot-stage and are not corrected. Rotatory powers were determined in Chf soln at room temp. Alumina refers to alumina Woelm deactivated with 5% water; silica refers to silica-gel (Merck) 140–230 Mesh. TLC were done with Kieselgel G (Merck) and spots were developed spraying the plates with a 2% soln of *p*-dimethylaminobenzaldehyde in 25% H_2SO_4 and heating at 120°.

For preparative TLC Kieselgel HF_{254} (Merck) was used. GLC was done on a Perkin-Elmer 800 chromatograph, using 6-feet columns.

Neutral fraction of frankincense. Frankincense grains (2 Kg) were refluxed with 1·5 l. ethyl ether. After 3 hr most of the soln was decanted and another liter of the same solvent added; the reflux was then continued for 3 hr. The combined extracts were shaken for 5 hr with a saturated aqueous soln (1·5 l.) of $Ba(OH)_2$, in which 120 g of solid $Ba(OH)_2 \cdot 8H_2O$ has been suspended.

The ethereal layer was separated by centrifugation and the solvent was removed in vacuum. The residue (105 g) was refluxed with an alcoholic soln (1·5 l.) of NaOH (3% w/v) for 3 hr. One liter of solvent was removed in vacuum and the residue was poured in water (3 l.).

The mixture was extracted with ether and the combined ethereal extracts were washed with water. The soln, dried over Na_2SO_4 and concentrated in vacuum, gave 70 g of neutral fraction.

Incensole (I). 20 g of neutral fraction were chromatographed over alumina (600 g) using benzene as eluent. Eleven fractions, each of 400 ml, were collected. Examination on TLC (benzene ether 8:2) showed that fractions 2-5 (5 g) contained incensole (I) and fraction 7-11 (0·7 g) contained a second substance, m.p. 164–165°. Fractions 2-5 were rechromatographed on silica (165 g) eluting with

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[16] See, for another example, G. V. Baddeley, P. R. Jefferies and R. W. Retallac, *Tetrahedron* 20, 1983 (1964).

hexane, hexane–ether 95:5, hexane–ether 9:1. The last solvent gave 1·5 g of almost pure material (examined by TLC). Distillation at 125°/0·1 mm Hg afforded an oil (one spot on TLC), which slowly changes into low-melting crystalline mass, which could not be induced to recrystallize from any solvent. Incensole is not preservable and decomposes slowly. It does not give any crystalline derivative (acetate, benzoate, 3,5-dinitrobenzoate). $[\alpha]_D = -77{\cdot}5°$ ($c = 1{\cdot}9$).

UV: no absorption above 210 mμ

IR: $\nu_{\max}^{(\mathrm{CCl_4})}$ (cm^{-1}) 3620 (—OH); 1670 (C═C); 1375, 1390 (CH_3—C—CH_3); 1050 (C—O)

NMR: 0·90 (6H, doublet, J = 6·5 c/s) (i-propyl); 1·02 (3H) (CH_3—C—O); 1·48 (3H), 1·61 (3H) (CH_3—C═); 3·18 (1H, doublet J = 10 c/s) (*H*C—OH); 5·06 (2H, broad signal) (HC═C)

(Found: C, 78·6; H, 11·1; $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·2%.)

Incensone (II). Incensole (I; 0·60 g) was added in pyridine (5 ml) to pyridine–CrO_3 complex prepared from pyridine (30 ml), water (1·5 ml) and CrO_3 (3 g). The mixture was allowed to stand for 50 hr at 30°.

Then, the mixture was poured in water and extracted with ether. The ethereal layer was washed with 2N HCl and water. The residue was purified by preparative TLC (eluent hexane–ether 7:3), yield g 0·35. Incensone (II) on sublimation, at 95° C/0·1 mm Hg, crystallizes in long needles, m.p. 42–44°, $[\alpha]_D = -20°$ ($c = 2$)

UV: (in EtOH) $\lambda_{\max} = 295$ mμ ($\varepsilon = 54$)

IR: $\nu_{\max}^{(\mathrm{CCl_4})}$ (cm^{-1}): 1720 (C═O); 1370, 1390 (CH_3—C—CH_3); 1040 (C—O)

NMR: 0·87 (3H, doublet J = 6·5 c/s), 0·91 (3H, doublet J = 6·5 c/s) (i-propyl); 1·27 (3H) (CH_3—C—O); 1·45 (3H), 1·52 (3H) (CH_3—C═); 4·93 (2H broad signal) (H—C═C)

(Found: C, 79·1; H, 10·40; $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6)

Mol. wt. (determined ojmometrically, using a Machrolab instrument and benzene as solvent): 303 ($C_{20}H_{32}O_2$ requires 304). The 2,4-dinitrophenylhydrazone crystallizes in plates from ethyl alcohol, m.p. 148–149°. (Found: C, 64·6; H, 7·8; N, 12·0; $C_{26}H_{36}O_5N_4$ requires C, 64·4; H, 7·5; N, 11·6%.)

Sodium borohydride reduction of ketone (II). Incensone (II; 400 mg), dissolved in MeOH (25 ml), containing one drop of 2N NaOH was treated with a soln of $NaBH_4$ (100 mg) in H_2O (2·5 ml), and the mixture was allowed to stand for 24 hr.

Water (100 ml) was added, and the pptd oil was extracted with ether. The ethereal soln was shaken with water and dried over Na_2SO_4. Examination of the residue on TLC showed the presence of two substances, one with the same R_f as that of incensole (I). Chromatographic separation on TLC (benzene:ether 8:2 as solvent) gave 85 mg of I and 162 mg of epi-incensole. Incensole (I) obtained in this way is identical in all respects (NMR and IR spectra) with an authentic sample.

Epi-incensole, purified by sublimation (130°/0·1 mm Hg) has m.p. 79–82°, $[\alpha]_D = -19{\cdot}2°$ ($c = 1{\cdot}16$).

IR: $\nu_{\max}^{(\mathrm{CCl_4})}$ (cm^{-1}): 3620 (—OH); 1670 (C═C); 1365, 1390 (CH_3—C—CH_3); 1060 (C—O)

NMR: 0·89 (3H, doublet J = 7 c/s) and 0·94 (3H, doublet J = 7 c/s) (i-propyl); 1·08 (3H) (CH_3—C—O); 1·57 (6H) (CH_3—C═); 3·63 (1H, 3 lines J ≃ 6 c/s) (*H*C—OH); 5·61 (2H, broad signal) (H—C═)

(Found: C, 78·5; H, 11·0; $C_{20}H_{34}O_2$ requires: C, 78·4; H 11·2%.)

Methyl laevulinate (IV) *by oxidation of incensole* (I). To a suspension of incensole (I) in water (20 ml), containing K_2CO_3 (140 mg), an aqueous soln (20 ml) of $NaIO_4$ (2·8 g) and $KMnO_4$ (100 mg) was added. The mixture was stirred for 18 hr at room temp.

Excess of oxidants was destroyed with sodium metabilsulfite, and the mixture was filtered and extracted with ether. The ethereal extract, after concentration, was treated with an ethereal soln of diazomethane. Excess of the reagent was destroyed with a drop of glacial AcOH and the soln was washed with $NaHCO_3$aq. Evaporation of the solvent left an oil, which, on gas-chromatography, showed the presence of a substance with the same retention time of an authentic sample of methyl laevulinate. The comparison was carried out using a "R" column (polipropylenglicol), $t = 140°$ (retention time 248 sec), a carbowax 20 M column, $t = 140°$ (retention time 165 sec) and a silicone SE 30 column, $t = 110°$, (retention time 170 sec).

Diketoester (V) *by oxidation of Incensole* (I). To a soln of incensole (I; 3 g) in acetone (300 ml), distilled over $KMnO_4$, finely divided $KMnO_4$ (3·5 g) was added under stirring at a temp between 16° and 20°. After 1 hr, a second portion of $KMnO_4$ (7·5 g) was added and the mixture was stirred for 4 hr at the same temp. Excess of the oxidant was destroyed by addition of 40% water soln of formaldehyde and most of the solvent was removed in vacuum.

The residue was treated with a 5% soln of Na_2CO_3 (150 ml) and heated for a short time on a water bath. The alkaline soln was filtered and extracted 3 times with ether; this extract was discarded. The aqueous layer was acidified at Congo red with diluted HCl and extracted 5 times with ether. The ethereal soln was shaken with water and dried over Na_2SO_4. Esterification with diazomethane, after concentration of the ethereal soln, gave a mixture of esters (2·3 g).

Gas-chromatographic analysis (column SE 30, programmed temp between 160° and 225°) showed the presence of 4 main substances, one of which was identical with methyl laevulinate.

The mixture was chromatographed on silica (g 120). Elution with hexane–AcOEt 8:2 afforded an oil (0·5 g), homogeneous on TLC and GLC. Distillation of this oil gave the pure diketoester (V), b.p. 136°/0·05 mm Hg.

UV: (in EtOH) $\lambda_{max} = 280$ mμ ($\varepsilon = 63$)

IR: ν_{max} (cm^{-1}): 1730 (C=O ester); 1715 (C=O ketone) (liquid film)

NMR: = 0·92 (3H, doublet J = 7 c/s) and 0·97 (3H, doublet J = 7 c/s) (i-propyl); 1·27 (3H) $(CH_3-\overset{|}{\underset{|}{C}}-O)$: 2·12 (3H) $(CH_3-\overset{|}{C}O)$; 3·58 (3H) (CH_3-O-)

(Found: C, 64·3; H, 8·5; $C_{16}H_{26}O_5$ requires C, 64·4; H, 8·8%.)

Subsequent elution with hexane: AcOEt 65:35 gave a second oily substance (g 0·35) which was not pure on TLC; it has not been further investigated.

Evidence for 1,4-*diketonic nature of* V. Diketoester (V; 25 mg) was dissolved in MeOH (3 ml) previously saturated with NH_3. After a few min the solvent was removed in vacuum. The residue was dissolved in AcOH (2 ml) and $(NH_4)_2CO_3$ (300 mg) was added. The mixture was gently refluxed for 10 min. The red brown soln was poured in water and neutralized with 30% NaOHaq.

Extraction with ether, followed by evaporation of the solvent, afforded a residue, which gave a red-purple colour with *p*-dimethylaminobenzaldehyde reagent.[17] The vapours of the residue turn red a splinter of pine wood moistened with conc. HCl.

Tetrahydroincensole (III) *by catalytic reduction of incensole* (I). Incensole (1 g) dissolved in AcOH (30 ml) was hydrogenated in the presence of pre-reduced PtO_2 (250 mg) at room temp and atm press. The hydrogenation stopped when two moles of H_2 had been adsorbed.

The mixture was filtered and the solvent evaporated in vacuum. The solid residue was dissolved in ether and the soln was shaken with dil NaOH and with water. The crystalline residue, although homogeneous on TLC, did not recrystallize from any solvent.

An analytical sample was purified by sublimation (120°/0·05 mm Hg), m.p. 94–100°.

NMR: 1·08 (3H) (CH_3-C-O); 3·40 (1H) $(H\overset{|}{\underset{|}{C}}-OH)$; no methyl signals within 1·4–1·7; no signals in the olefinic protons region. (Found: C, 77·4; H, 12·3; $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3.)

Unsaturated ketone (VII). Tetrahydroincensole (III; 1 g) dissolved in a mixture (30 ml) of $AcOH-H_2SO_4$ 12N (10:3) was refluxed for 1 hr.

The mixture was poured in water and extracted with ether. The ethereal extract was shaken with water and dried over Na_2SO_4. Evaporation of the solvent left an oily residue (0·9 g) which showed on GLC (carbowax 20 M column, $t = 195°$) 2 mains peaks (only one spot on TLC).

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[17] F. Feigl: *Spot tests in Organic Analysis* p. 289. Elsevier, Amsterdam (1960).

The mixture was submitted to preparative GLC (Aerograph 705, 6 feet column of Carbowax 20 M) collecting the substance with the highest retention time.

Distillation of this product at 95°/0·1 mm Hg yielded pure VII, which crystallizes on standing, m.p. 43–49° (yield: 140 mg)

IR: $\nu_{max}^{(CCl_4)}$ (cm^{-1}): 1710 (C═O); no bands in the —OH region and between 1000–1100.

NMR: (100 Mc): 0·89 (doublet J = 7 c/s) and 0·91 (doublet J = 7 c/s) (CH_3—CH); 1·05 (doublet, J = 7 c/s) (CH_3—$\overset{|}{C}$H—CO); 1·60 (6H) $\left(\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>\!C—\right)$; 2·30 ($CH_3$—$\overset{|}{C}H$—CO) (broad signal): see also footnote 12

(Found: C, 82·1; H, 12·1; $C_{20}H_{36}O$ requires C, 82·1; H, 12·40%.)

Cembrane by reduction of ketone (VII). Amalgamated Zn[18] was added to VII (120 mg) dissolved in 30 ml of a mixture of glacial AcOH–conc. HCl–EtOH 3:2:2. The mixture was refluxed for 4 hr; then, a further 15 ml conc. HCl were added during 4 hr and the refluxing was continued for 36 hr. After cooling, water (30 ml) was added and the mixture extracted 4 times with light petroleum (30–50°). The soln was shaken with water and the solvent evaporated at atm press. Distillation of the residue at 151°/1 mm Hg gave an oil which was almost pure on GLC and presented the same retention time of an authentic sample of cembrane (430 sec on carbowax 20 M column; t = 160°, 430 sec on silicone SE 30 column; t = 215°).

Mass spectra were recorded with a LKB 9000 gas chromatograph-mass spectrometer (chromatographic column packed with silicone Se 30, t = 150°).

The spectrum of cembrane, obtained here, was identical with the spectrum of a sample of synthetic cembrane.

Acknowledgments—We are greatly indebted to Dr. I. D. Entwistle (University of Exeter) and to Dr. R. A. W. Johnstone (University of Liverpool) for providing the sample of synthetic cembrane, to Dr. A. Melera (Varian Research Laboratories) for determination of NMR spectrum at 100 Mc and double resonance experiments. We thank Dr. T. Salvatori (SNAM, Research Laboratories, Milan) for mass spectra, Dr. C. Iavarone (this Institute) for NMR spectra at 60 Mc and Italian C.N.R. for financial support.

[18] Prepared according to E. L. Martin: The Clemmensen reduction in *Organic Reactions* Vol. I; p. 163. Wiley, New York (1942).