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THE STRUCTURE OF INCENSOLE-OXIDE

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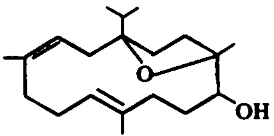
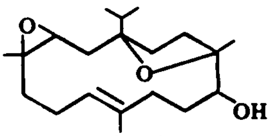
Abstract—A new diterpene, incensole-oxide (I), closely related to incensole, has been isolated from frankincense in small amounts. The chemical and physico-chemical data showing the position of the oxirane ring, support the structure I.

The structure of a new macrocyclic diterpene, incensole, isolated from frankincense, the resin produced by *Boswellia carteri*, has been reported.[1]



Incensole



Incensole-oxide (I)

A second substance (I), closely related to incensole, has been isolated from the same source and we suggest the name incensole-oxide.

Incensole oxide (I) m.p. 164–165° $[\alpha]_D$ −48°, has the molecular formula $C_{20}H_{34}O_3$, according to the composition and mol. wt. (322) deduced from its mass spectrum. It gives a crystalline monoacetate (II), m.p. 118–120°.

The spectroscopic properties are similar to those of incensole. The IR spectrum of I in addition to the OH absorbance (3450 cm^{-1}) shows an intense band at 1050 cm^{-1}, attributable to the 5-membered cyclic ether.[1] The NMR spectrum shows the presence of an isopropyl group (two doublets at 0·92 and 0·95 δ, $J = 6{\cdot}5$ c/s) and a secondary alcoholic function (doublet at 3·40 δ, $J = 10$ c/s, shifted downfield ($\simeq$ 1 ppm) in the corresponding acetate).[2] Unlike incensole, two of the three detectable Me groups are fixed on carbons each carrying an oxygen atom, while the third is on a double bond. Only an olefinic proton ($\delta = 5{\cdot}23$) is present. Finally, centered at 3·03 δ (1H) four lines may be attributed to an epoxide proton.

Chemical evidence of the presence of an epoxide ring was obtained by treating the incensole-oxide (I) with LAH under forced conditions yielding a more polar compound (III), $C_{20}H_{36}O_3$, $[\alpha]_D$ −17°, m.p. 132–133·5°. Since the nucleophilic displacement occurs on a less substituted carbon,[3] the formation of a tertiary alcoholic function was expected. The NMR spectrum of III (solvent pyridine) when compared with the spectrum of I (same solvent) shows the downfield shift of a Me signal (the more shielded one, from 1·20 to 1·30 δ)* as well as the disappearance of the four peaks due to the epoxide proton, in accordance with expectation.

The diole III has a double bond, since it absorbs one molecule of hydrogen on

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* This shift, associated with the cleavage of the epoxide, can be justified in terms of ring current.[4]

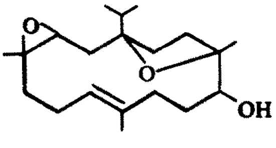
catalytic reduction,* giving a mixture of epimeric dihydro derivatives (unsharp m.p.) $C_{20}H_{38}O_3$, easily distinguishable by TLC.

Further similarities between incensole and the oxide (I) are apparent in the spectra of incensone oxide (IV), $C_{20}H_{32}O_3$ $[\alpha]_D$ −65° m.p. 102–103°, obtained by chromium trioxide oxidation of I. In the IR spectrum there are no absorbances in the OH region; as in the case of incensone (the corresponding ketone from incensole),[1] the C=O stretching vibration is at 1718 cm^{-1}, and a strong band is still present at 1044 cm^{-1} (ethereal bridge).

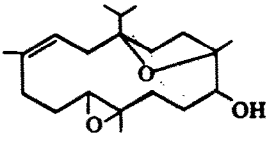
As in the NMR spectrum of the parent alcohol, the spectrum of ketone IV shows the presence of two methyls fixed on oxygen bearing carbons; but the less shielded methyl—presumably attached to the carbon carrying the ethereal oxygen—appears shifted downfield in the case of the ketone, while the position of the other methyl is unchanged. The first methyl is therefore in α-position with respect to the carbonyl.

The data presented so far—the presence of a secondary alcoholic function, an oxirane ring, a double bond, and the probable presence of an etheral bridge—confirm the close relationship between incensole and incensole-oxide (I), the main difference being the presence in I of an oxirane ring instead of a double bond. Chemical evidence was obtained by treating incensole with *p*-nitroperbenzoic acid† which yields a product identical in all respects (m.p., IR, NMR spectra) with I.

Consequently, incensole oxide (I) can only have one of the two following structures:

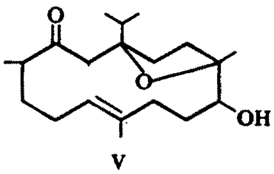


A≡(I)

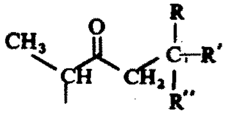


Compound I, treated with 50% perchloric acid gives the ketone V‡ (IR, CO band at 1700 cm^{-1}), $C_{20}H_{34}O_3$, m.p. 138–139°, $[\alpha]_D$ 161°, formed by rearrangement of the epoxide ring, since its NMR spectrum shows the doublet ($J = 7$ c/s) due to the Me in α-position to a carbonyl group ($\delta = 1{\cdot}07$) but not the singlet related to the Me fixed on the oxirane ring. In addition, an AB pattern at 2·57 δ is clearly distinguishable at 100 Mc, and the lack of further splitting indicates the partial structure VI.

The ketone V has therefore the structure given, and consequently, incensole-oxide (I) has the structure A



V



R, R', R'' ≠ H

VI

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* Catalytic reduction of incensole oxide (I) affords a mixture, possibly due to the cleavage of the epoxide: however, this reaction has not been further investigated.

† Incensole reacts very slowly with perbenzoic acid, so that we preferred to use the *p*-nitro derivative.[5]

‡ The cleavage of epoxide ring under these conditions usually leads to the diole.[6] The observed rearrangement could be related to the steric hindrance, towards the entering nucleophile, presented by the "back side" of the oxirane ring. This statement is also consistent with the difficulties encountered in the cleavage of the epoxide, by means of LAH.

In order to obtain chemical evidence of the position of the carbonyl in respect to ethereal oxygen, we first tried to promote a β-elimination, catalysed by bases. The failure of these experiments may be due to the steric hindrance of the C atom adjacent to carbonyl, which is in α-position in respect to the i-propyl group.

In order to attempt a similar reaction under acidic conditions, the double bond was reduced yielding two epimeric dihydro derivatives, $C_{20}H_{36}O_3$, (VII) m.p. 120–133° and (VIII) m.p. 129–130°.

After several attempts, the action of perchloric acid on VII* gave an oily compound (IX), $C_{20}H_{36}O_3$, in good yield.

The mass spectrum of IX shows a molecular ion at *m/e* 324– and significant peaks at *m/e* 281 and 253. High resolution measurement† shows that the *m/e* 281 peak ($M^+ - 43$) is produced by two different ions, having the composition $C_{17}H_{29}O_3$ and $C_{18}H_{33}O_2$ (intensity ratio $\simeq$ 7:2). Hence, the molecule can lose an acetyl or an i-propyl group. The *m/e* 253 peak corresponds to the loss of 43 + 28 mu (i-propyl + CO).

These data agree with the hypothesis that the molecule is no longer cyclic, but has a methyl-ketone group at one end of the chain and an isopropyl ketone group‡ at the other end.

The NMR spectrum (Fig. 1) shows the signal due to CH_3CO (sharp signal at 1·75 δ);

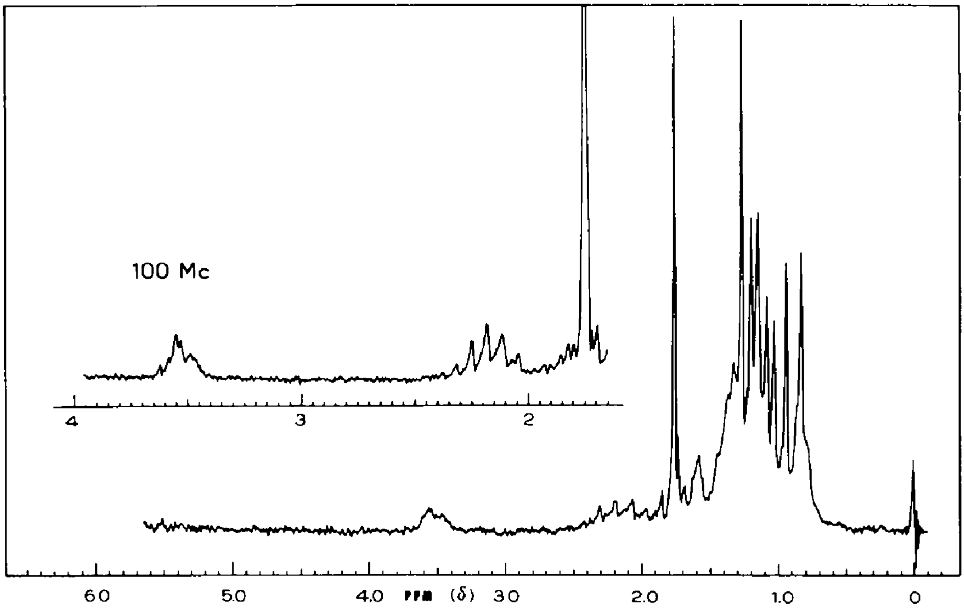

Fig. 1 NMR spectrum of IX in benzene (60 and 100 Mc).

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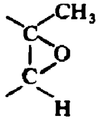
* We used also the epimeric mixture for these experiments obtaining a product with the same general properties. However, we preferred to repeat the reaction using one isomer, in order to have a product showing a sharper NMR spectrum.

† Using an AEI MS-9, with an apparent resolution of $\simeq$ 10-000. We are very grateful to Mrs. Sharon M. Jones (Department of Chemistry, University of California, Los Angeles) for the assistance in these measurements.

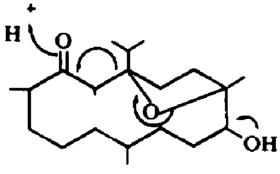
‡ α-cleavage of ketons, as well as the CO loss of the oxigenated fragment, are well known processes.[7]

at 100 Mc a quintuplet at 2·15 δ is easily recognizable even if overlapped with the signal of another proton. By irradiating this region, the signal due to the isopropyl tends to become a singlet, as well as the doublet centered at 0·90 δ. Then, one of the α-carbonyl protons belongs to the isopropyl, while the other one is coupled with a methyl. Moreover, the spectrum indicates the nature of the third oxygen atom. A sharp Me signal at 1·27 δ and a broad signal at 3·52 δ* agrees with the presence of the group:†

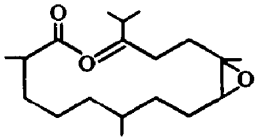


Finally, at higher field (0·81 δ) a broad signal is present: no doubt due to the Me fixed on the carbon flanked by two $—CH_2—$ groups[10].

Spectroscopic data supports the structure of compound IX, which is consistent with the following transformation path



VII



IX

The opening of the carbocyclic ring, understandable in terms of a retroaldol type reaction, which correlates the position of the carbonyl in respect to the ethereal oxygen, demonstrates the structure of I.

EXPERIMENTAL

IR spectra were recorded with a Perkin–Elmer 257. NMR spectra were determined in $CDCl_3$ soln with a Varian A-60, unless otherwise stated. All chemical shifts are quoted in δ-values, using TMS as internal standard. M.ps and rotatory powers were determined as described before; similarly TLC and preparative chromatography, as well as column chromatography was carried out using the same materials and equipment.[1]

Incensole-oxide (I). The neutral fraction of frankincense (20 g) chromatographed over alumina (600 g) using benzene as eluent, gave eleven fractions (400 ml each). The oily residue of fractions 7–11 (0·7 g) was dissolved in pet. ether, and crystallized after standing at −10° for 24 hr, (0·3 g). Several crystallizations from light petroleum 80–100° gave pure incensole-oxide (I) as plates, m.p. 164–165° $[\alpha]_D$ −48° (c = 1·08); IR: ν_{max} (cm^{-1}): 3450 (—OH); 1380, 1390 ($CH_3—C—CH_3$); 1050 (C—O) (in Nujol); NMR: 0·92 (3H, doublet J = 6·5 c/s), 0·95 (3H, doublet, J = 6·5 c/s) (i-propyl); 1·08 (3H) $(\mathrm{CH_3{-}\underset{|}{C}\overset{O}{{-}{-}}\underset{|}{C}})$; 1·18 (3H) $(\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O})$; 1·70 (3H) $(\mathrm{CH_3{-}\overset{|}{C}{=}})$; 3·03 (1H), (four lines) $(\mathrm{H\underset{|}{C}\overset{O}{{-}{-}}\underset{|}{C}})$; 3·40 (1H, doublet J = 10 c/s) $(\mathrm{\overset{|}{\underset{|}{C}}\underline{H}\ OH})$; 5·23 (1H, broad signal $(\mathrm{H{-}\overset{|}{C}{=}})$; NMR (Me resonances in pyridine): 0·98 (3H, doublet,

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* The resonance of epoxide protons generally lies between 2·8 and 3·5 δ.[8]

† Actually, we expected in this reaction a rearrangement similar to that observed in the case of incensole,[1] leading to a keto-group. However, the formation of epoxides from glycols (or closely related systems) has been observed in some instances under acidic conditions.[9]

$J = 6{\cdot}5$ c/s), 1·00 (3H, doublet, $J = 6{\cdot}5$ c/s) (i-propyl; 1·20 (3H) ($\mathrm{CH_3{-}\underset{|}{C}\overset{O}{\frown}\underset{|}{\overset{\diagup}{C}}}$); 1·35 (3H) ($\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$); 1·68 (3H) ($\mathrm{CH_3{-}\overset{|}{C}{=}}$). (Found: C, 74·3; H, 10·5; $C_{20}H_{34}O_3$ requires; C, 74·5; H, 10·6%).

Incensole oxide acetate (II). To I (100 mg), dissolved in pyridine (3 ml), Ac_2O (0·3 ml) was added. After 50 hr at room temp, the mixture was worked up in the usual way and gave a residue which crystallized (twice) from light petroleum 60–80° as small prisms, m.p. 118–120°; NMR: 4·87 (1H, doublet, $J = 9$ c/s) ($\mathrm{\overset{|}{\underset{|}{C}}\underline{H}{-}O{-}Ac}$). (Found: C, 72·6; H, 10·2; $C_{22}H_{36}O_4$ requires: C, 72·5; H, 10·0%).

LAH *Reduction of incensole oxide* (I): *diole* (III). Incensole oxide (I) (240 mg) was refluxed in THF (10 ml) with LAH (60 mg) for 12 hr. More LAH (60 mg) was added and the reflux continued for 24 hr.

Excess of the reagent was destroyed by careful addition of THF—H_2O. The reaction mixture was then filtered, and the solvent removed *in vacuo*: the residue dissolved in ether and washed with 1N HCl and water. After drying over Na_2SO_4 the solvent was removed *in vacuo*. Examination of the residue by TLC (benzene–ether 8:2 as eluent) showed the presence of two substances, one of them having the same R_f of the starting material. Separation by preparative TLC (same eluent) gave crude III (yield: 140 mg) as small needles from benzene–light petroleum 80–100°; m.p. 132–132·5 $[\alpha]_D$ −17° ($c = 1{\cdot}02$); IR: ν_{max} (cm^{-1}): 3350 (—OH); 1030 (C—O) (in Nujol); NMR: (in pyridine) 0·90 (3H, doublet, $J = 7$ c/s), 0·95 (3H, doublet, $J = 7$ c/s) (i-propyl): 1·32 (3H) $\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$): 1·35 (3H) ($\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$): 1·74 (3H) ($\mathrm{CH_3{-}\overset{|}{C}{=}}$): 3·77 (1H, broad) ($\mathrm{\overset{|}{\underset{|}{C}}\underline{H}{-}OH}$); 5·02 (1H, broad) ($\mathrm{H{-}\overset{|}{C}{=}}$). (Found: C, 73·9; H, 11·3; $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%).

Catalytic reduction of diole (III). Diole III, dissolved in EtOH (10 ml) was hydrogenated at atm press and room temp, in presence of Pd/C (10%, 40 mg), previously saturated with H_2. The reduction stopped when one mole H_2 had been absorbed. After filtration and removal of the solvent, the residue, examined by TLC (benzene–ether 8:2 as eluent), proved to be a mixture of two substances, with very close R_f values. The mixture was recrystallized from benzene–light petroleum 80–100°, m.p. 142–145·5° (sintering from 130°). (Found: C, 73·7; H, 11·6; $C_{20}H_{38}O_3$ requires: C, 73·6; H, 11·7%).

Incensone oxide (IV). Incensole-oxide (I; 0·23 g), dissolved in pyridine, was added to CrO_3–pyridine complex, prepared from pyridine (11 ml), CrO_3 (1·1 g) and water (0·16 ml). The clear soln was allowed to stand for 48 hr at 27°. After the usual work up the residue was purified on preparative TLC (benzene–ether 9:1 as eluent). The main substance (with highest R_f), ketone IV, was collected (yield: 0·17 g) and purified by sublimation (95°/0·05 mm Hg). Needles from MeOH, 102–102·5°; $[\alpha]_D$ −65° ($c = 0{\cdot}88$); IR: $\nu_{max}^{(CCl_4)}$ (cm^{-1}): 1718 (C=O); 1412 ($\mathrm{\overset{O}{\overset{\|}{C}}{-}C\genfrac{}{}{0pt}{}{\diagup H}{\diagdown H}}$); 1370, 1388 ($\mathrm{CH_3{-}C{-}CH_3}$); 1044 (C—O); NMR: 0·90 (3H, doublet, $J = 7$ c/s), 0·95 (3H doublet, $J = 7$ c/s) (i-propyl); 1·08 (3H) ($\mathrm{CH_3{-}\underset{|}{C}\overset{O}{\frown}\underset{|}{\overset{\diagup}{C}}{-}}$); 1·34 (3H) ($\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$); 1·70 (3H) ($\mathrm{CH_3{-}\overset{|}{C}{=}}$); 5·09 (1H, broad) ($\mathrm{H{-}\overset{|}{C}{=}}$). (Found: C, 74·7; H, 10·0; $C_{20}H_{32}O_3$ requires: C, 75·0; H, 10·0%).

Incensole-oxide (I) *by oxidation of incensole*. To a soln of incensole (5 g) in CCl_4–t-butanol (1:1), *p*-nitroperbenzoic acid (3 g) was added in four portions, during 10 min, under stirring and cooling (−20°). The stirring was continued for 10 min, at the same temp. Then, the reaction mixture was poured into a ice-cold sat $NaHCO_3$aq (300 ml), and the organic materials extracted with ether. After washing with water, and drying over Na_2SO_4, the solvents were removed *in vacuo*. The residue (5·8 g), examined on TLC (benzene–ether 6:4 as eluent) contained a little unreacted incensole and the incensole-oxide (I) and other substances with lower R_f values. By chromatography on Silica (200 g), using benzene–ether (8:2) as eluent, after a pre-run, four fractions (500 ml each) containing a crystalline residue, were collected. Several crystallizations from light petroleum 80–100° yielded the pure compound, m.p. 164–165° (alone or in mixture with an authentic sample), yield: 1 g; the NMR and IR spectra of this compound are undistinguishable from those of I isolated from the resin.

Reaction of incensole oxide (I) *with* $HClO_4$: *ketone* (V). A solution of I (0·75 g) in ethanol-free $CHCl_3$ (18 ml) was vigorously shaken with $HClO_4$ 50% (3 ml) at 0° for 30 min. The reaction mixture was poured into 2N Na_2CO_3 and extracted with ether. The ether soln was washed with water and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica with benzene–ether 95:5 as eluent. The first 3 fractions (25 ml each) contained I and other impurities; subsequent elution with the same solvent gave 12 fractions, containing V (0·52 g). It was purified by sublimation (115°/0·1 mm Hg) and recrystallization as long needles from light petroleum 60–80°, m.p. 138–139° $[\alpha]_D$ +161 (c = 1·0); IR: $\nu_{max}^{(CCl_4)}$ (cm^{-1}): 3618 (OH); 1700 (C═O) 1389, 1372 ($\mathrm{CH_3{-}C{-}CH_3}$); 1030 (C—O); NMR: 0·88 (3H, doublet, J = 7 c/s), 0·92 (3H, doublet J = 7 c/s) (i-propyl); 1·07 (3H, doublet J = 7 c/s) ($\mathrm{CH_3{-}\overset{|}{C}H{-}\overset{|}{C}O}$); 1·08 (3H) ($\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$); 1·67 (3H) ($\mathrm{CH{-}\overset{|}{\underset{|}{C}}{=}}$); 2·57 (2H, AB system, J = 13 c/s) ($\mathrm{{-}CH_2{-}\overset{|}{C}O}$); 3·50 (1H, broad doublet J = 10 c/s) ($\mathrm{\underset{|}{C}\underline{H}{-}OH}$); 5·20 (1H, broad) ($\mathrm{H\underset{|}{C}{=}}$). (Found: C, 74·5; H, 10·6; $C_{20}H_{34}O_3$ requires: C, 74·7; H, 10·8%).

Catalytic reduction of ketone (V). Ketone V (0·8 g) dissolved in EtOH 95° (80 ml), was hydrogenated, at atm press and room temp, in presence of previously saturated Pd/C (5%, 400 mg). The reduction stopped when one mole H_2 had been absorbed. After filtration and removal of most of the solvent, the residue, diluted with water, was extracted with ether. Evaporation of the solvent gave a residue, which proved by TLC (benzene–ether 8:2 as eluent) to be a mixture of two substances, having very close R_f values. The separation was carried out by chromatography on silica (50 g), using benzene–ether 95:5 as eluent. Fraction 9–13 (50 ml each) contained the pure less polar isomer VII (200 mg), while fractions 20–24 contained VIII (280 mg). *The dihydroketone* VII crystallized from light petroleum 60–80° in irregular prisms m.p. 120–133°; IR: $\nu_{max}^{(CCl_4)}$ (cm^{-1}): 3630 (—OH); 1705 (C═O); 1375, 1350 ($\mathrm{CH_3{-}\underset{|}{C}{-}CH_3}$); 1073 (C—O); NMR: (100 Mc in C_6H_6) 0·72 (3H, doublet, J = 7 c/s) ($\mathrm{C\underline{H}_3{-}\overset{|}{\underset{|}{C}}H}$); 0·95 (6H, doublet J = 7 c/s) (i-propyl) 1·00 (3H, doublet J = 6·5 c/s) ($\mathrm{C\underline{H}_3{-}\overset{|}{C}H{-}\overset{|}{C}{=}O}$); 1·20 (3H) ($\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$); 2·39 (2H, four lines, AB system); 3·07 (1H, doublet) ($\mathrm{{-}\overset{|}{\underset{|}{C}}\underline{H}{-}OH}$); no signals in the olefinic protons region. (Found: C, 74·3; H, 11·3; $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%). *The epimer* VIII crystallized in prisms from light petroleum 60–80° m.p. 129–130°; IR: $\nu_{max}^{(CCl_4)}$ (cm^{-1}): 3630 (—OH); 1700 (C═O); 1374, 1100, 1030 (C—O); NMR: 0·90 (6H, doublet J = 7 c/s) (i-propyl); 0·98 (3H, doublet J = 7 c/s) ($\mathrm{C\underline{H}_3{-}\overset{|}{C}H{-}\overset{|}{C}O}$); 1·15 (3H) ($\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}{-}O}$); 2·58 (2H, two lines, central part of an AB system); 3·48 (1H, broad) ($\mathrm{\overset{|}{\underset{|}{C}}\underline{H}{-}OH}$); no signals in the olefinic protons region. (Found: C, 74·2; H, 11·2; $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%).

Diketo epoxide (IX). Dihydroketone VII (380 mg), dissolved in EtOH free $CHCl_3$ (12 ml) was shaken vigorously for 15′ at room temp, with $HClO_4$ (70%, 4 ml). The mixture was poured into 2N Na_2CO_3 and extracted with ether. The organic layer was washed with water and dried. The residue, examined by TLC (hexane–ether 7:3 as eluent), contained a new substance (with higher R_f) and a small amount of the starting material. Operating on a preparative scale on oily substance IX was isolated (yield 230 mg). The product obtained in this way was pure on GLC (carbowax column, t = 195° and SE 30 column, t = 230°). It is an oil, b.p. 120°/0·1 mm Hg) (Hickmann); IR: ν_{max} (cm^{-1}): 1712 (C═O); 1385, 1368 ($\mathrm{CH_3{-}\underset{|}{C}{-}CH}$); 930, 870, 836 (liquid film); NMR: (methyls resonances) 0·88 (3H, broad) ($\mathrm{C\underline{H}_3{-}\overset{|}{\underset{|}{C}}H}$); 1·00 (6H, doublet, J = 7 c/s) (i-propyl); 1·08 (3H, doublet, J = 7 c/s) ($\mathrm{C\underline{H}_3{-}\overset{|}{C}H{-}\overset{|}{C}O}$) 1·41 (3H) ($\mathrm{CH_3{-}\overset{|}{\underset{|}{C}}\overset{O}{\text{—}}\overset{|}{\underset{|}{C}}}$); 2·12 (3H)

(CH_3—CO); NMR (methyls resonances in benzene solution): see text. (Found: C, 74·1; H, 11·0; $C_{20}H_{36}O_3$ requires: C, 74·0; H, 11·2%).

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