Tetrahedron, 1958, Vol. 3, pp. 160–167. Pergamon Press Ltd., London

THE CHEMISTRY OF SANTONIN—V*

SOME REDUCTION PRODUCTS OF 11β(H)-SANTONIN

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(*Received* 28 *January*, 1958)

Abstract—Three tetrahydro-11β(H)-santonins have been obtained by the hydrogenation of 11β(H)-santonin over palladised charcoal. Two of these tetrahydro-11β(H)-santonins were previously obtained by Clemo. They have now been shown to have a *trans*-A/B ring-fusion, by relating them to the stable *trans*-A/B ring-fused tetrahydrosantonin. A third tetrahydro-11β(H)-santonin (*cis*-A/B ring-fusion) and 1:2-dihydro-11β(H)-santonin have been isolated in small quantities from the same reaction. A 4:5-dihydro-11β(H)-santonin has been isolated from the hydrogenation of potassium 11β(H)-santoninate in methanol over a platinum catalyst. The preparation of two hexahydro-11β(H)-santonins is described.

THE stereochemistry of the reduction products of santonin (I) has been the subject of several recent investigations.[1,2,3,4,5] Though the Japanese authors originally gave the opposite assignment,[1] it is now agreed[2,3,4] that the so called α-tetrahydrosantonin† has a *trans*-A/B ring-fusion while β-tetrahydrosantonin has a *cis*-A/B ring-fusion.

This result is of interest, since the main product of the hydrogenation of santonin thus has the *trans*-A/B ring-fusion. In the steroid 4-en-3-ones hydrogenation gives varying results. For example, cholestenone yields predominantly the *cis*-fused coprostanone,[7,8] whilst testosterone affords the *trans*-fused androstane-17β-ol-3-one. Amongst simpler compounds one finds that 4:10-dimethyloctal-4-en-3-one is hydrogenated over palladised charcoal to *trans*-4:10-dimethyldecal-3-one.[2] It might be argued that differences in stereochemical reduction of these systems can be traced to the nature of attached groups, in that these might inhibit the absorption of either the α- or β-face of the ring system on the catalyst.

It seemed to us worth while to study the hydrogenation of 11β(H)-santonin, which differs from santonin only in the configuration at C_{11}. In santonin, the 11β-methyl group should favour absorption of the α-face of the molecule on the catalyst, and hence products having a *trans*-A/B ring-fusion should be formed.

In 11β(H)-santonin (II), the 11α-methyl group might be expected to discourage

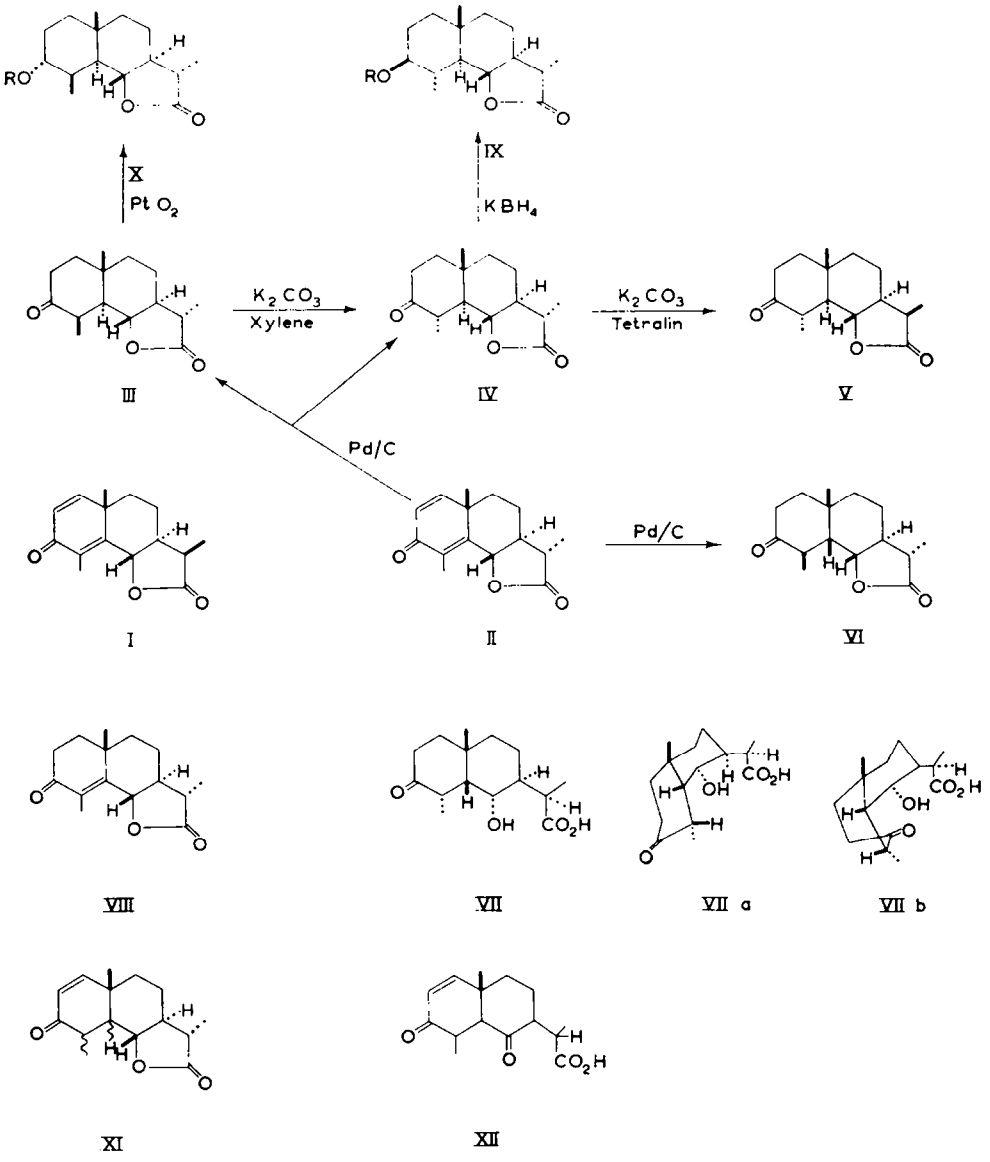
* Part IV. W. Cocker, K. Crowley, J. T. Edward, T. B. H. McMurry and E. R. Stuart, *J. Chem. Soc.* 3416, (1957).

† The prefixes α and β are used in this context in the manner employed by the earlier workers in this field.[6] Elsewhere we use the nomenclature of Cocker and McMurry[3].

[1] M. Yanagita and A. Tahara, *J. Org. Chem.* **20**, 959 (1955); A. Tahara, *J. Org. Chem.* **21**, 442 (1956).
[2] M. Yanagita and R. Futaki, *J. Org. Chem.* **21**, 949 (1956); M. Yanagita and H. Ogura, *J. Org. Chem.* **22**, 1092 (1957).
[3] W. Cocker and T. B. H. McMurry, *J. Chem. Soc.* 4549 (1956).
[4] B. Riniker, Thesis, E. T. H., Zurich (1955); C. Djerassi, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **78**, 6362 (1956).
[5] Ö. Kováks, V. Herout, M. Horák and F. Šorm, *Chem. Listy*, **49**, 1856 (1955); *Coll. Czech. Chem. Commun.* **21**, 225 (1956).
[6] Cf. Sir John Simonsen and D. H. R. Barton, *The Terpenes* (Vol. III) p. 292. Cambridge University Press (1952).
[7] H. Grasshof, *Z. Physiol. Chem.* **223**, 249 (1934).
[8] A. Butenandt, K. Tscherning and G. Hanisch, *Ber. Dtsch. Chem. Ges*, **68**, 2097 (1935).

absorption on the α-face, and lead to the formation of greater amounts of products with *cis*-A/B ring-fusion.

Accordingly, we have investigated the hydrogenation of 11β(H)-santonin under various conditions, and we have found that the configuration at C_{11} has little influence on the manner of reduction.



Clemo[9] showed that reduction of 11β(H)-santonin with hydrogen afforded a mixture of two tetrahydro compounds, m.p. 125–126° and 207–208°, which on reduction by the Clemmensen method gave the same deoxytetrahydro-11β(H)-santonin.

[9] G. R. Clemo, *J. Chem. Soc.* 1343 (1934).

This result implied that the two compounds had the same type of ring-fusion and hence could only differ in configuration at C_4, the less stable isomer being epimerised at this centre under the strongly acid conditions of the reaction (cf. Kováks *et al.*[5]).

We have hydrogenated 11β(H)-santonin in acetic acid and have obtained the two tetrahydro compounds described by Clemo in a total yield of 75 per cent. From the products of the same reduction we have also isolated a third tetrahydro compound, m.p. 140·5–141·5°, which like the other two is dextrorotatory. In addition a dihydro-11β(H)-santonin was also isolated.

The isomer, m.p. 207–208°, proved to be less stable at C_4 than the compound, m.p. 125–126°, for the former was readily converted into the latter either (*a*) by treatment, in the cold, with a solution of toluene-*p*-sulphonic acid in acetic acid,[5] or (*b*) with potassium carbonate in boiling xylene.[10] The lower-melting compound thus has an equatorial methyl group at C_4 (cf. Cocker and McMurry[3] and Kováks *et al.*[5]). The nature of the A/B ring junction was demonstrated by epimerisation of the lower-melting compound at C_{11}, thus affording 3-oxo-5:11α(H),4:6β(H)-eudesman-6:13-olide (α-tetrahydrosantonin) (V), whose A/B ring junction is known to be *trans* fused.[1,2,3,4,5,6] Hence we can now state that the higher- and lower-melting tetrahydro-11β(H)-santonins, first prepared by Clemo,[9] are, respectively, 3-oxo-4:5α(H), 6:11β(H)-eudesman-6:13-olide (III) and 3-oxo-5α(H)4:6:11β(H)-eudesman-6:13-olide (IV). It is interesting to note that in order to isomerise (IV) to (V) we had to employ potassium carbonate in boiling tetrahydronaphthalene, whereas the isomerisation of 11β(H)-santonin to santonin can be effected with potassium carbonate in boiling xylene.[10]

The third, and new, tetrahydro-11β(H)-santonin (m.p. 140·5–141·5°) that we now describe must obviously have *cis*-A/B ring-fusion, and, since it is stable to potassium carbonate in boiling xylene, we conclude that it has an equatorial methyl group at C_4, and this must have the β-configuration. The new tetrahydro compound is thus 3-oxo-4α(H),5:6:11β(H)-eudesman-6:13-olide (VI).

In an earlier paper in this series,[3] we pointed out that in the corresponding santonin series, the *cis*-A/B ring-fused tetrahydrosantonin (β-tetrahydrosantonin[6]) and the derived hydroxy acid have opposite configurations at C_4. Lactonisation of the hydroxy acid performed by heating at 200° effects epimerisation at C_4, a configurational change that can be reversed when the lactone is hydrolysed. We assigned the α (axial) configuration to the 4-methyl group in the lactone and β (equatorial) in the acid. These assignments were based upon the following facts. Reduction of the tetrahydrosantonin over Adams's catalyst gave a hexahydro compound, also derived in low yield by hydrogenation of santonin itself. Since the major product of the latter reaction was a hexahydrosantonin (*trans*-A/B fused system) having *cis* arrangement of hydrogen atoms at C_4 and C_5, it was considered likely that the minor product of reduction (*cis*-A/B fused system) would also have *cis* arrangement of hydrogen atoms at C_4 and C_5. That is, these hydrogen atoms would have β configuration, resulting in an axial 4α-methyl group. However, this argument is not valid. It has been shown that the *cis*-A/B fused tetrahydrosantonin has a rotatory dispersion curve similar to that of a 3-oxo-5β-steroid, implying that the 4-methyl group is β (equatorial)[4]. The 4-methyl group in the tetrahydrosantoninic acid (VII) must consequently be α-orientated.

[10] W. Cocker and T. B. H. McMurry, *J. Chem. Soc.* 4430 (1955).

The stability of C_4 with its α-orientated methyl group in the hydroxy acid can be explained if it is assumed that it does not have the normal chair conformation of ring A as in (VIIA), but rather a boat conformation as in (VIIB) in which the 4-methyl group becomes equatorial.* The latter structure will be stabilised by hydrogen bonding between the 6-hydroxyl and the 3-oxo groups.

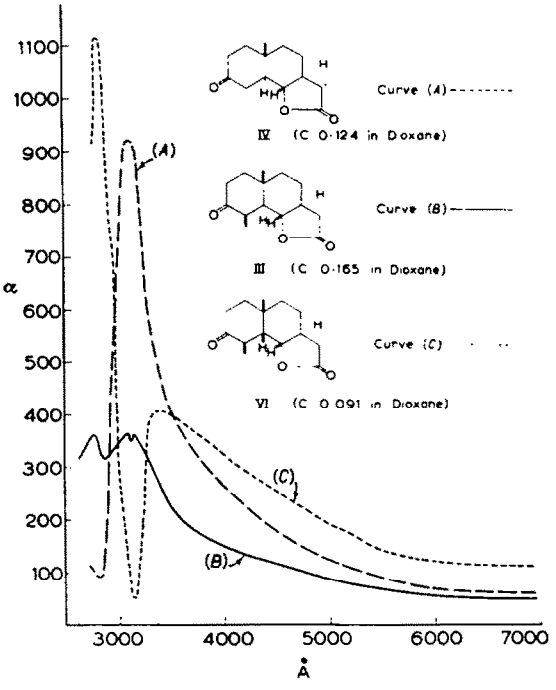


FIG. 1. Rotary dispersion of tetrahydro-11β(H)-santonins

That the assignment of structure to compounds (III), (IV) and (VI) is correct is shown by inspection of their rotatory dispersion curves, which were made available to us through the kindness of Professor Djerassi. Fig. 1 shows that the tetrahydro-11β(H)-santonin, m.p. 125–126° (IV) (curve A) has a typical *trans*-A/B fused 3-oxo-5α-steroid rotatory dispersion curve, which is similar to that of 3-oxo-5:11α(H)4:6β(H)-eudesman-6:13-olide (V).[4,6] Similarly the dispersion curves of the tetrahydro

* While this paper was in course of preparation, Banerji *et al.*[11] propounded a similar view. We first mentioned our view to Professor Djerassi early in 1957, after he had pointed out to us that the rotatory dispersion curve of the *cis*-tetrahydrosantoninic acid mentioned above was like that of a *trans*-fused 3-oxo-5β-steroid.

[11] J. C. Banerji, D. H. R. Barton and R. C. Cookson, *J. Chem. Soc*, 5041 (1957).

compounds, m.p. 207–208° (III), and 140–141·5° (VI) (curves B and C, respectively) are closely similar to those of 3-oxo-4:5:11α(H),6β(H)-eudesman-6:13-olide and 3-oxo-4:11α(H),5:6β(H)-eudesman-6:13-olide, respectively.[3,4]

It is also interesting to compare the molecular rotations of the corresponding tetrahydrosantonins and 11β(H)-santonins and these are set out in Table 1.

It is obvious from Table 1 that the two sets of compounds show similar trends in molecular-rotation changes, thus implying similar stereochemical relationships.

TABLE 1. MOLECULAR ROTATIONS OF TETRAHYDROSANTONINS AND TETRAHYDRO-11β(H)-SANTONINS

Santonin	$[M]^D$	Santonin	$[M]^D$
3-Oxo-5:11α(H),4:6β(H)-eudesman-6:13-olide (V)	+ 70°	3-Oxo-5α(H),4:6:11β(H)-eudesman-6:13-olide (IV)	+205°
3-Oxo-4:5:11α(H),6β(H)-eudesman-6:13-olide	+179°	3-Oxo-4:5α(H),6:11β(H)-eudesman-6:13-olide (III)	+295°
3-Oxo-4:11α(H),5:6β(H)-eudesman-6:13-olide	+ 25°	3-Oxo-4α(H),5:6:11β(H)-eudesman-6:13-olide (VI)	+166°

The dihydro-11β(H)-santonin mentioned above proved to be the 1:2 dihydro compound (VIII). This structure is assigned, since in the ultra-violet region it shows a maximum at 2470 Å (log ε 4·18); this is close to the expected value[12] of 2520 Å. A second peak at 3150 Å (log ε 1·8), and peaks at 1780 (lactone), 1670 (keto), 1615 (C=C) and 1430 cm^{-1} (CH_2 next to C=O in a 6-membered ring) in the infra-red region support the αβ-unsaturated ketone structure. The ketone also forms a 2:4-dinitrophenylhydrazone, which shows typical maximum absorption at 3850 Å (log ε 4·56).

The dihydro compound was obtained in greater yield by hydrogenation of 11β(H)-santonin in ethanol over an activated Raney nickel catalyst[13] at room temperature and pressure.

When 3-oxo-5α(H),4:6:11β(H)-eudesman-6:13-olide (IV) was reduced with potassium borohydride, 3β-hydroxy-5α(H),4:6:11β(H)-eudesman-6:13-olide (IX, R = H) was obtained in good yield. Reaction with acetic anhydride and pyridine gave the corresponding acetate with *positive* increment in molecular rotation (Table 2), and hence[14,15,16,17] the hydroxyl and its acetate must be β (equatorial) orientated, a result to be expected of the method of preparation of the alcohol.

When 11β(H)-santonin was reduced in acetic acid over Adams's catalyst, it afforded 3α-hydroxy-4:5α(H),6:11β(H)-eudesman-6:13-olide (X, R = H). The orientation of the hydroxyl follows from the *negative* increment in molecular rotation (Table 2) on acetylation. From the method of preparation it may be inferred that

[12] L. F. Fieser and M. Fieser, *Natural Products Related to Phenanthrene* (3rd ed.) p. 190. Reinhold, New York (1949).
[13] A. A. Pavlic and H. Adkins, *J. Amer. Chem. Soc.* **68**, 1471, (1946).
[14] W. Klyne and W. M. Stokes, *J. Chem. Soc.* 1979 (1954).
[15] W. M. Stokes and W. Bergmann, *J. Org. Chem.* **17**, 1194 (1952).
[16] J. A. Mills, *Chem. & Ind.* 218 (1953).
[17] D. H. R. Barton and A. Nickon, *J. Chem. Soc.* 4665 (1954).

the hydroxyl is axial, and this is confirmed by the fact that the alcohol is obtained when the *trans*-fused tetrahydro-11β(H)-santonin (III) is reduced over platinic oxide in acetic acid.

Reduction of potassium 11β(H)-santoninate in methanol over Adams's catalyst affords the *cis*-fused tetrahydro compound (VI), a result to be expected by analogy with the santonin series.[3] At the same time the hexahydro compound (X) was obtained and a 4:5-dihydro compound 3-oxo-4:5ξ(H),6:11β(H)-eudesm-1-en-6:13-olide (XI).

TABLE 2. MOLECULAR ROTATIONS OF HEXAHYDRO-11β(H)-SANTONINS AND ACETATES

Santonin	$[M]_D$ of alcohol	$[M]_D$ of acetate	Δ_1*
3β-Hydroxy-5α(H),4:6:11β(H)-eudesman-6:13-olide (IX, R = H)	+302°	+315°	+13°
3α-Hydroxy-4:5α(H),6:11β(H)-eudesman-6:13-olide (X, R = H)	+237°	+164°	−73°

* Δ_1 is defined as suggested by Klyne and Stokes.[14]

The double bond is located in the 1:2-position, since the substance shows maxima at 2280 Å (log ε 3·89) and 3180 Å (log ε 1·51), in close agreement with the spectrum of 3:6-dioxoeudesm-1-en-13-oic acid (XII).[2,12]

The formation of (X) in small yield in the reduction of potassium 11β(H)-santoninate is probably due to the presence of some unhydrolysed santonin in the methanolic solution of the salt.

EXPERIMENTAL

Ultra-violet spectra were (unless otherwise stated) measured for ethanolic solutions with a Beckman DU instrument. Infra-red spectra were measured in chloroform solutions with a Hilger 800 double-beam instrument. $[\alpha]_D$ refer to chloroform solutions.

Hydrogenation of 11β(H)-*santonin* (cf. Clemo[9])

A mixture of 11β(H)-santonin (12 g), 10% palladised charcoal (2 g) and acetic acid (100 ml) was stirred in an atmosphere of hydrogen for 24 hr. Filtration and removal of solvent gave a solid, which was fractionally crystallised from ethyl acetate to give 3-oxo-4:5α(H),6:11β(H)-eudesman-6:13-olide (III) as rhombs (3·9 g), m.p. 206–208°, $[\alpha]_D^{15}$ +118·1° (*c*, 0·9) [max. at 1780 (lactone), 1710 cm^{-1} (ketone)] (Found: C, 72·1; H, 8·8. Calc. for $C_{15}H_{22}O_3$: C, 72·0; H, 8·9 per cent).

Removal of the mother-liquors from the crystallisation of (III), and two further crystallisations of the residue from ethanol, gave 3-oxo-5α(H),4:6:11β(H)-eudesman-6:13-olide (IV) (5·2 g), m.p. 125–126°, $[\alpha]_D^{15}$ +81·9° (*c*, 1·33) (max. at 1780, 1714 cm^{-1}) (Found: C, 71·6; H, 9·1. Calc. for $C_{15}H_{22}O_3$: C, 72·0; H, 8·9 per cent).

Concentration of the ethanolic mother-liquors from (IV) gave a solid (0·6 g), which on further recrystallisation from ethanol gave 3-*oxo*-4α(H),5:6:11β(H)-*eudesman*-6:13-*olide* (VI) as rhombs, m.p. 140·5–141·5°, $[\alpha]_D^{15}$ +66·6° (*c*, 1·75) (max. at 1784, 1720 cm^{-1}) (Found: C, 71·9; H, 9·0. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·9 per cent).

In a second hydrogenation the above-mentioned mother-liquors deposited a

mixture of rhombs and hexagonal plates. The latter, separated by hand picking, were recrystallised from ethanol to give 3-*oxo*-6:11β(H)-*eudesm*-4*en*-6:13-*olide* (VIII), m.p. 121°, $[\alpha]_D^{15}$ + 112·5° (*c*, 1·2) [λ_{max} 2470 Å (log ε 4·18), 3150 Å (log ε 1·80); 1780 (lactone), 1670 (keto), 1630 cm^{-1} (C=C)] (Found: C, 72·6; H, 8·1. $C_{15}H_{20}O_3$ requires C, 72·55; H, 8·1 per cent). The 2:4-*dinitrophenylhydrazone* was obtained as orange-red plates from ethanol, m.p. 240° [λ_{max} 2610 Å, (log ε 4·04), 3850 Å (log ε 4·56)] (Found: C, 58·0; H, 5·5. $C_{21}H_{24}O_6N_4$ requires C, 58·9; H, 5·6 per cent).

Conversion of 3-*oxo*-4:5α(H),6:11β(H)-*eudesman*-6:13-*olide* (III) *to* 3-*oxo*-5α(H),-4:6:11β(H)-*eudesman*-6:13-*olide* (IV)

Method (a). The keto-lactone (III) (0·92 g), freshly ignited potassium carbonate (1 g) and dry xylene (50 ml) were heated under reflux for 30 hr. Filtration and removal of the solvent from the filtrate gave crude 3-oxo-5α(H),4:6:11β(H)-eudesman-6:13-olide (IV), which on crystallisation from ethanol was obtained (0·78 g), m.p. 124–125° undepressed on admixture with an authentic specimen.

Method (b). A mixture of the keto-lactone (III) (1·0 g), toluene-*p*-sulphonic acid (0·9 g) and acetic acid (10 ml) was set aside for 16 hr. Dilution with water and crystallisation of the product from ethanol gave the ketone (IV) (1·0 g), m.p. 125–126°.

Conversion of 3-*oxo*-5α(H),4:6:11β(H)-*eudesman*-6:13-*olide* (IV) *into* 3-*oxo*-5:11α(H),-4:6β(H)-*eudesman*-6:13-*olide* (V)

Method (a). A mixture of the ketone (IV) (1 g), anhydrous potassium carbonate (1 g) and dry tetrahydronaphthalene (50 ml) was heated under reflux for 4 hr. Filtration and removal of the tetrahydronaphthalene from the filtrate gave a product, which, after being washed with light petroleum and crystallised from ethyl acetate–light petroleum (boiling range 60–80°), gave 3-oxo-5:11α(H),4:6β(H)-eudesman-6:13-olide (0·3 g) as needles, m.p. 155°, undepressed by admixture with an authentic specimen.[3]

Method (b). The desired epimerisation also took place, but in small yield when the ketone (IV) (0·3 g) was heated under reflux for 4 hr with sodium methoxide, from sodium (2 g) in methanol (30 ml). Removal of methanol, dilution of the residue with water, acidification and extraction with ether gave an oil, which became partly solid on trituration with light petroleum. Chromatography in benzene–ether mixture (4 + 1) on Woelm brand acid alumina afforded a solid product, m.p. 116–140°. Crystallisation from ethyl acetate–light petroleum gave 3-oxo-5:11α(H),4:6β(H)-eudesman-6:13-olide (10 mg), m.p. and mixed m.p. 155°.

3-*Oxo*-6:11β(H)-*eudesm*-4-*en*-6:13-*olide* (VIII)

11β(H)-Santonin (3 g) was hydrogenated for 50 min in ethanol (250 ml) at room temperature and pressure in presence of Raney nickel (W_5) (1 g).[13] Filtration and removal of the solvent afforded crude 3-oxo-6:11β(H)-eudesm-4-en-6:13-olide (VIII), which crystallised (1 g) from ethyl acetate, m.p. 122–123°, identical with the material described above.

Reduction of 3-*oxo*-5α(H),4:6:11β(H)-*eudesman*-6:13-*olide* (IV)

3β-*Hydroxy*-5α(H),4:6:11β(H)-*eudesman*-6:13-*olide* (IX, R = H). The ketone (IV) (2 g) in methanol (30 ml) was mixed with potassium borohydride (0·12 g) in water (5 ml) and set aside for 1 hr. The solution was diluted with water and acidified, when it yielded a solid product (2 g), which on crystallisation from aqueous ethanol

gave 3β-*hydroxy*-5α(H),4:6:11β(H)-*eudesman*-6:13-*olide* (IX, R = H) as needles, m.p. 154°, $[\alpha]_D^{15}$ + 119·8° (*c*, 1·1) (Found: C, 71·35; H, 9·8. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6 per cent). Its *acetate* (IX, R = Ac) was obtained (0·15 g) when the alcohol (0·2 g) was heated on the water bath for 2 hr with a mixture of acetic anhydride (5 ml) and pyridine (5 ml). The acetate crystallised from aqueous ethanol as plates, m.p. 99–100°, $[\alpha]_D^{16}$ + 107·2° (*c*, 0·44) [max. at 1777 cm^{-1} (lactone); 1740, 1263 cm^{-1} (acetate)] (Found: C, 69·7; H, 8·8. $C_{17}H_{26}O_4$ requires C, 69·4; H, 8·9 per cent).

Hydrogenation of 11β(H)-*santonin over platinic oxide*

3α-*Hydroxy*-4:5α(H),6:11β(H)-*eudesman*-6:13-*olide* (X, R = H). 11β(H)-Santonin (2 g) in glacial acetic acid (150 ml) was hydrogenated at room temperature and pressure over Adams's catalyst (0·1 g) until there was no further uptake of hydrogen. Filtration and removal of solvent gave a solid product, which after two recrystallisations from ethyl acetate–light petroleum gave 3α-*hydroxy*-4:5α(H),6:11β(H)-*eudesman*-6:13-*olide* (X, R = H) as needles (0·6 g), m.p. 146–147°, $[\alpha]_D^{15}$ + 94° (*c*, 0·99) (Found: C, 71·6; H, 9·3. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6 per cent). Acetylation of the alcohol with acetic anhydride and pyridine afforded its *acetate* (X, R = Ac), which crystallised from ethyl acetate, m.p. 170–172°, $[\alpha]_D^{15}$ + 55·7° (*c*, 1·1) [max. at 1774 cm^{-1} (lactone); 1727, 1264 cm^{-1} (acetate)] (Found: C, 69·3; H, 8·5. $C_{17}H_{26}O_4$ requires C, 69·4; H, 8·9 per cent).

Reduction of 3-*oxo*-4:5α(H),6:11β(H)-*eudesman*-6:13-*olide* (III). Hydrogenation of (III) (0·37 g) in acetic acid (100 ml) over platinic oxide (0·11 g) gave an oil, which on acetylation with acetic anhydride and pyridine gave the acetate (X, R = Ac) (0·32 g), m.p. and mixed m.p. 170–172°.

Hydrogenation of potassium 11β(H)-*santoninate.* 11β(H)-Santonin (10 g) was heated under reflux for 20 min in methanol (200 ml) containing potassium hydroxide (4 g), cooled and hydrogenated at room temperature and pressure over Adams's catalyst (0·32 g). After 18 hr the mixture was filtered, concentrated to 30 ml, acidified with dilute hydrochloric acid and then heated under reflux for 1 hr to effect lactonisation. Removal of solvents gave an oil, which on standing in ether gradually deposited crystals (0·85 g). Crystallisation from aqueous ethanol and then from ethyl acetate gave pure 3-oxo-4α(H),5:6:11β(H)-eudesman-6:13-olide (VI), m.p. and mixed m.p. 140°.

Evaporation of the ethereal mother-liquors gave an oil (8·3 g), which was repeatedly extracted with boiling light petroleum (boiling range 60–80°). The early extracts gave in all about 1 g of (VI), m.p. 138–139°. Later extracts deposited a solid (0·32 g), which after crystallisation from ethyl acetate had m.p. 147–148°, identical with (X).

In a similar experiment, but when previously used platinum black (0·3 g) (from Adams's catalyst) was employed, the ether solution mentioned above deposited crystals (0·7 g). Crystallisation first from ethyl acetate after treatment with charcoal and then twice from ethanol gave 3-*oxo*-4:5ξ(H),6:11β(H)-*eudesm*-1-*en*-6:13-*olide* (XI) as needles, m.p. 207–208°, $[\alpha]_D^{15}$ −20·7° (*c*, 0·8) [max. at 2280 Å (log ε 3·89), 3180 Å (log ε1·51); 1778 cm^{-1} (lactone), 1685 cm^{-1} (ketone)] (Found: C, 72·1; H, 8·2. $C_{15}H_{20}O_3$ requires C, 72·55; H, 8·1 per cent.

Acknowledgements—We are grateful to Messrs. T. & H. Smith, Ltd., for gifts of the santonins and to the Medical Research Council of Ireland for financial support. One of us (N. J. H. D.) thanks the Government of the Republic of Ireland for a maintenance allowance.

We also thank Professor Djerassi for providing us with the rotatory dispersion curves.