Tetrahedron, 1965, Vol. 21, pp. 1167 to 1173. Pergamon Press Ltd. Printed in Northern Ireland

TERPENOIDS LXVII*

SYNTHESIS OF A KETODICARBOXYLIC ACID RELATED TO ELEMOL AND EPIDIHYDROEUDESMOL

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(*Received* 15 *December* 1964)

Abstract—11-Oxo-2,3-seco-7α(H)-12-noreudesmane-2,3-dioic acid (XVI) and epidihydroeudesmol (XXI) have been synthesized starting from santonin (V).

THERE has been considerable interest in the biogenesis of the crystalline monocyclic sesquiterpene alcohol, elemol (I),[1] the precursor of which may be the monocyclic alcohol (II),[2,3] which, however, has not so far been isolated. Saussurea lactone (III) having the elemane carbon skeleton is formed readily during the pyrolysis of dihydrocostunolide (IV).[4] The structure and stereochemistry of saussurea lactone has been proved to be III.[4]

(—)-α-Santonin (V), the absolute configuration of which has been established by X-ray studies[5] and other investigations,[6] has the eudesmane carbon skeleton. It was considered of interest to correlate V with compounds having the closely related elemane carbon skeleton. One reason for choosing santonin as the starting point for this investigation is the location of the carbonyl group at C_3 which can be utilized to bring about the fission of the C_2—C_3 bond necessary for the conversion of the eudesmane to the elemane carbon skeleton. The synthesis of tetrahydrosaussurea lactone from santonin has been achieved,[7] and its conversion to the ketodicarboxylic acid (XVI related to elemol is presented in this communication.

Santonin (V) was converted to the keto-acid (VII) by reduction with lithium in liquid ammonia.[8,9] Reduction of the keto acid (VII) with lithium in liquid ammonia furnished the saturated keto acid (VIII)$^+$ whose methyl ester was purified by regeneration from its semicarbazone. The keto ester (X) exhibits bands at 1730 and 1704 cm^{-1}. The UV spectrum of the keto ester (X) as well as its semicarbazone show that it is free from the methyl ester of the starting material (VII). Two new asymmetric centres have

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* Communication No. 748 from the National Chemical Laboratory, Poona-8, India.

[1] V. Sykora, J. Cerny, V. Herout, J. Pliva and F. Sorm, *Coll. Czech. Chem. Comm.* **19**, 124, 566 (1954); **20**, 220 (1955).

[2] L. Ruzicka, *Experientia* **9**, 357 (1953).

[3] J. B. Hendrickson, *Tetrahedron* **7**, 82 (1959).

[4] A. S. Rao, A. Paul, Sadgopal and S. C. Bhattacharyya, *Tetrahedron* **13**, 319 (1961).

[5] J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.* 335 (1962).

[6] W. Cocker and T. B. H. McMurry, *Tetrahedron* **8**, 181 (1960); M. Nakazaki and H. Arakawa, *Proc. Chem. Soc.* 151 (1962).

[7] D. M. Simonovic, A. S. Rao and S. C. Bhattacharyya, *Tetrahedron* **19**, 1061 (1963).

[8] H. Brunderer, D. Arigoni and O. Jeger, *Helv. Chem. Acta* **39**, 858 (1956).

[9] W. Cocker, B. Donnelly, H. Gobinsinjh, T. B. H. McMurry and M. A. Nisbet, *J. Chem. Soc.* 1261 (1963).

been introduced in the conversion of the acid (VII) to the ester (X). The stereochemistry shown in the formula is assigned to the keto ester (X) for the following reasons: (a) the keto ester (X) is not epimerized by heating under reflux with methanolic hydrochloric acid which is known to bring about the epimerization of related ketones having the unstable configuration at C_4.[11] Hence the methyl group of the ester (X) at C_4 is in the thermodynamically stable configuration; (b) similar reductions[12] of α,β-unsaturated ketones structurally related to the keto acid (VII) are known to give *trans*-decalone derivatives, and by analogy the stereochemistry of the acid (VIII) and consequently its methyl ester (X) are correctly represented by the formulae shown in the figure.

The optical rotatory dispersion curve of the keto ester (X) is in good agreement with the stereochemistry. It exhibits a positive Cotton effect curve which is expected on the basis of octant rule.[13] Djerassi and Klyne[14] have reported the rotatory dispersion curves of a number of decalones of the type (XI) which have a β-oriented (axial) angular methyl group, and a β-oriented (equatorial) C_7 side chain and a methyl substituent at C_4. Some of these compounds have an additional α-(equatorial) substituent at C_8 which is not expected to make a large contribution to the rotatory dispersion curve. Amongst these compounds only *trans*-decalones having α-(equatorial) C_4 methyl group exhibit a positive Cotton effect curve of large amplitude. The ketoester (X) also exhibits a positive Cotton effect curve of large amplitude ($a = +63$).

The keto group of the keto ester (X) was protected by conversion to the ethylene ketal (XII) which on reaction with phenyl magnesium bromide and subsequent treatment with acetic acid, furnished the keto alcohol (XIII). The dehydration product (XIV) of XIII was condensed with benzaldehyde in the presence of sodium hydroxide to give the benzylidine derivative (XV) whose spectral properties (λ_{max} 290 mμ, (log ε 4·1) ν_{max} 1672 cm^{-1} are in agreement with the proposed structure. Ozonolysis of XV followed by oxidation furnished the keto dicarboxylic acid (XVI) which was esterified with diazomethane to give the corresponding methyl ester (XVII). During the synthesis of the keto dicarboxylic acid (XVI) and just as the correlation with elemol was nearing completion, Halsall *et al.*[15] published the absolute configuration of elemol.† These authors had synthesised the same keto dicarboxylic acid (XVI) by a different route and succeeded in correlating it with elemol by converting it to the triol (XVIII), which was identical with the triol prepared by the hydroboration of elemol (XIX).

† Dauben Hayer, Schwarz and McFarland[10] reported the formation of keto acid (IX) during the hydrogenation of (−)-santonin-C. However, the stereochemistry[4] at C_4 and C_8 for the acid so prepared has not been established.

† The absolute configuration of elemol has also been established recently by A. D. Wagh, S. K. Paknikar and S. C. Bhattacharyya.[11] Tetrahedron **20,** 2647 (1964).

[10] W. G. Dauben, W. K. Hayes, J. S. Paul Schwar and J. W. McFarland, *J. Amer. Chem. Soc.* **82,** 2232 (1960).

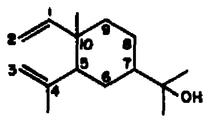
[11] O. Kovacs, V. Herout, M. Horak and F. Sorm, *Coll. Czech. Chem. Comm.* **21,** 225 (1956); M. Yanagita and A. Tahara, *J. Org. Chem.* **20,** 959 (1958).

[12] J. A. Findlay, W. A. Henry, T. C. Jain, Z. Valenta, K. Wiesner and C. M. Wong, *Tetrahedron Letters,* 869 (1962); D. H. R. Barton, C. H. Robinson, *J. Chem. Soc.* 3045 (1954); C. Djerassi and G. H. Thomas, *J. Amer. Chem. Soc.* **79,** 3835 (1957).

[13] W. Moffitt, R. B. Woodward, A. Moscourtz, W. Klyne and C. Djerassi, *J. Amer. Chem. Soc.* **83,** 4013 (1961).

[14] C. Djerassi and W. Klyne, *J. Chem. Soc.* 4249 (1962).

[15] T. G. Halsall, D. W. Theobald and K. B. Walshaw, *J. Chem. Soc.* 1029 (1964).



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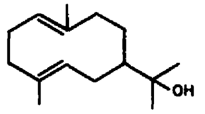

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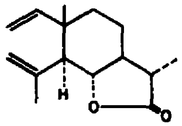

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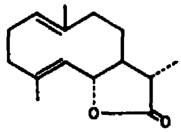

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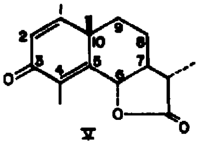

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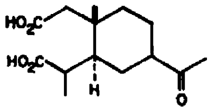

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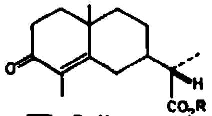
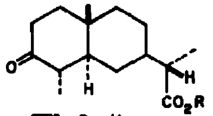
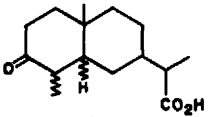


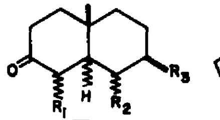
VII , R = H
VIIa , R = CH₃



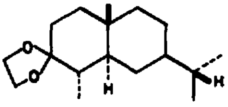
VIII , R = H
X R = CH₃



IX



XI



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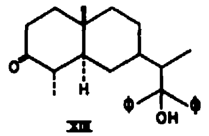

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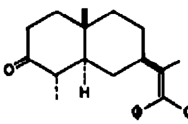

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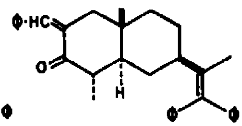

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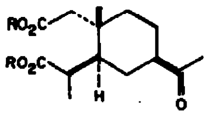
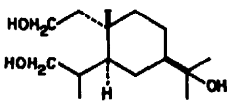
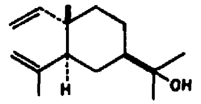


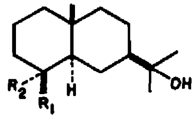
XVI R = -H
XVII R = CH₃



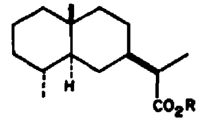
XVIII



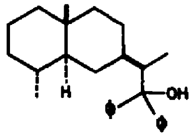
XIX



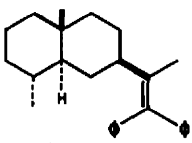
XX R₁ = Me; R₂ = H
XXI R₁ = H; R₂ = Me



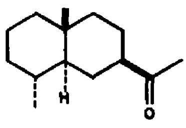
XXII R = H
XXIII R = CH₃



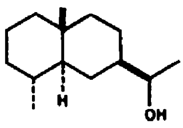
XXIV



XXV



XXVI



XXVII

With the keto ester (X) of known stereochemistry available as an intermediate in the synthesis described above we turned our attention to a convenient preparation of 4-epidihydroeudesmol. Hydrogenation of eudesmol with Pd catalyst gives a nearly 1:1 mixture of dihydroeudesmol (XX) and its 4-epimer (XXI). Isolation of the pure epidihydroeudesmol from this mixture could be accomplished only on a limited scale through preparative gas liquid chromatography.[16] Since fairly large quantities of pure XXI were required in connection with other investigations, it was synthesized from the keto ester (X) by the following method:

Wolff-Kishner reduction of (X) furnished the acid (XXII) whose methyl ester on reaction with phenyl magnesium bromide followed by dehydration and ozonolysis gave a mixture of the C_{14} ketone (XXVI) and benzophenone. Since a separation of these

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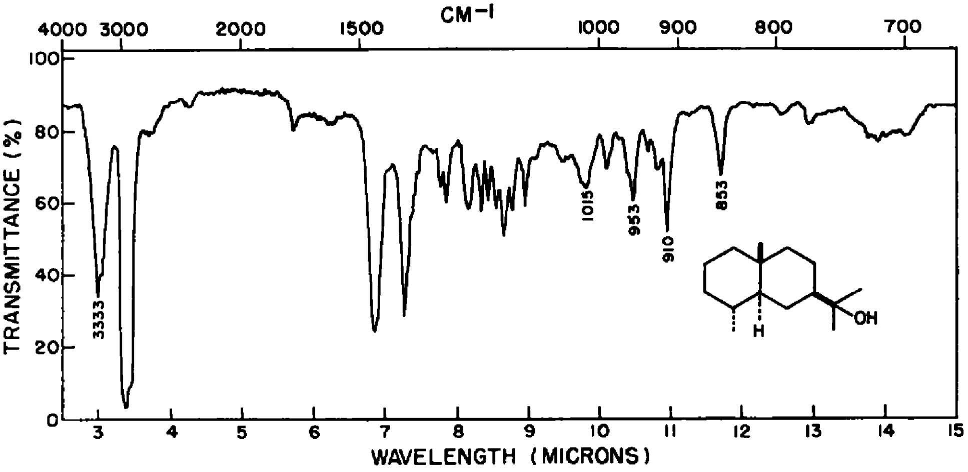
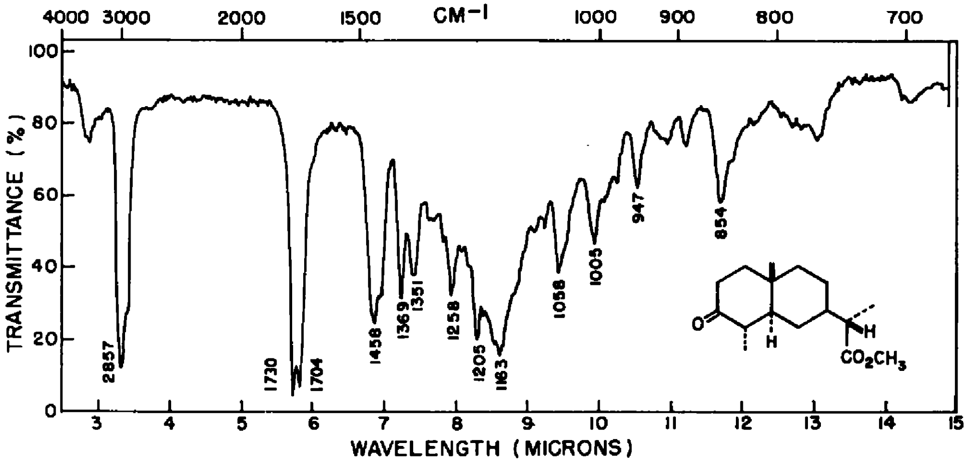
[16] E. von Rudloff and H. Erdtman, *Tetrahedron* **18**, 1315 (1962).





two ketones was expected to be difficult, the mixture was reduced with LAH in the presence of aluminium chloride. Under these conditions, the C_{14} ketone (XXVI) was converted to the corresponding secondary alcohol (XXVII) and benzophenone yielded the hydrocarbon, diphenylmethane which was readily separated from the secondary alcohol by column chromatography. The secondary alcohol was oxidized with Jones reagent[17] to the corresponding ketone (XXVI) which was purified by regenerating it from its semicarbazone. The ketone (XXVI) on reaction with methyl magnesium iodide furnished 4-epidihydroeudesmol (XXI) having properties (m.p. and rotation) identical with that of a specimen prepared by von Rudloff *et al.**

* We could not make a direct comparison of our preparation of 4-epidihydroeudesmol with the sample reported in literature[16] since von Rudloff was unable to supply a sample. However, all the four possible dihydroeudesmols having the β-configuration of angular methyl group at C_{10} and β-configuration of C_7 side chain are properly characterized and the m.p. and rotation of these four epimers are significantly different from each other to enable one to make a choice.

[17] C. Djerassi, R. R. Engle and A. Bowers, *J. Org. Chem.* **21**, 1547 (1956).

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. Elemental analyses were performed by Mr. Pansare and colleagues in the microanalytical section of our laboratory. UV spectra were taken in alcoholic solution with a Beckman DK-2 instrument and IR spectra on a Perkin–Elmer infracord by Gopinath and Deshpande. Optical rotations were determined in $CHCl_3$ at room temp (25–30°).

3-*Oxo*-11*β*(*H*)-*eudesm*-4-*en*-13-*oic acid* (VII). To liquid ammonia (2 l.) was added with stirring Li (3 g) and a solution of santonin (10 g) in dry tetrahydrofuran (100 ml). The reaction mixture was stirred for 3 hr and kept overnight. It was then treated with cold dil. H_2SO_4 till it was acidic to congo red. The product was separated into acidic and neutral portions. The acidic portion (9 g) on crystallization from acetone and hexane yielded pure VII (8 g), m.p. 123–124°, $(\alpha)_D$ +110 (*c*, 4·9). Lit.[8,9] records m.p. 125–126°, $(\alpha)_D$ +114° for VII. (Found: C, 72·06; H, 9·07%. $C_{15}H_{22}O_3$ requires: C, 71·97; H, 8·86%.) The IR spectrum (in $CHCl_3$) showed bands at: 2976, 1709, 1661, 1608, 1449, 1418, 1377, 1351, 1232, 1179, 1085 and 1017 cm^{-1}. In one of the above experiments, the product did not solidify. Since the product showed the presence of an hydroxyl group (IR spectrum), it was oxidized with Jones reagent[17] and VII was readily isolated as a crystalline solid.

Semicarbazone of methyl-3-*oxo*-4,11*β*(H), 5α(H) *eudesman*-13-*oate* (X). To liquid ammonia (500 ml) was added with stirring Li (200 mg) and an ethereal solution (100 ml) of VII (2 g) under anhydrous conditions. After stirring for ½ hr, NH_4Cl was added gradually till the blue colour was discharged. After keeping overnight, the reaction mixture was acidified with cold dil. H_2SO_4. Extraction with ether furnished a viscous acidic material (1·977 g) which was esterified with diazomethane. The IR spectrum of the ester showed bands for an hydroxyl group (3448 cm^{-1}) as well as a keto group (1736 cm^{-1}). Chromatography of the product on alumina (gr. III) gave X which was contaminated with appreciable amounts of (ca. 20%) VIIa (ε value of earlier chromatographic fractions 2,000). After a few trials the following procedure was found satisfactory. The esterified product (450 mg), derived from VII (420 mg) which on the basis of IR and UV data was a mixture of X, corresponding hydroxy ester and VIIa (with the former two constituents predominating) was oxidized with Jones reagent.[17] The oxidized product (no hydroxyl absorption in the IR spectrum) (300 mg) was dissolved in alcohol (2 ml) and heated for a few min. on a steam bath and a saturated aqueous solution of semicarbazide hydrochloride (300 mg) and sodium acetate (400 mg) added. After keeping the reaction mixture at room temp. for 3 days, a crystalline semicarbazone (350 mg) m.p. 150–160° separated out. Recrystallization from dil. alcohol (3 ×) furnished the pure semicarbazone (95 mg), m.p. 172° of X. (Found: C, 63·45; H, 9·43; N, 13·3; $C_{17}H_{29}O_3N_3$ requires: C, 63·13; H, 9·04; N, 12·99%.) λ_{max} 228 mμ (log ε 4·14). The IR spectrum of the semicarbazone of (X) (in nujol) showed bands at: 3571, 3356, 3012, 1748, 1701, 1669, 1587, 1453, 1408, 1385, 1355, 1212, 1190, 1157, 1136, 1092, 1042, 1020, 980, 846 and 766 cm^{-1}.

Methyl-3-*oxo*-4,11*β*(H), 5α(H)-*eudesman*-13-*oate* (X). The semicarbazone m.p. 172° (3·4 g) of X was dissolved in EtOH (10 ml) and heated on steam bath for 3 hr with 100 ml pet. ether (60–80°) and oxalic acid (3 g) dissolved in water (10 ml). After cooling the reaction mixture, extraction with pet. ether, washing with water, drying and evaporation of solvent furnished X (2·82 g), b.p. 170–180° (bath)/0·3 mm, $(\alpha)_D$ +12·96 (*c*, 4·6). The optical rotatory dispersion taken in MeOH (*c*, 0·24); $[\phi]_{400\,m\mu}$ +140, $[\phi]_{333}$ +2640, $[\phi]_{288}$ 0, $[\phi]_{266}$ −3660, $[\phi]_{239}$ −2050, $[\phi]_{222}$ −2215. (Found: C, 72·06; H, 9·54. $C_{16}H_{26}O_3$ requires: C, 72·14; H, 9·84%.) The IR spectrum showed bands at: 2857, 1730, 1704, 1458, 1359, 1351, 1258, 1205, 1163, 1058, 1005, 947 and 854 cm^{-1}.

Methyl-3-*oxo*-11*β*(H)-*eudesm*-4-*en*-13-*oate* (VIIa). This was prepared from VII by esterification with diazomethane, b.p. 170–180° (bath)/0·3 mm, $(\alpha)_D$ +100° (*c*, 4·59), λ_{max} 248 mμ (log ε 3·97). (Found: C, 72·20; H, 9·23. $C_{16}H_{24}O_3$ requires: C, 72·69; H, 9·15%.) The IR spectrum (liquid film) showed bands at: 1736, 1668, 1615 cm^{-1}.

Ketal (XII). A mixture of VII (2·8 g), benzene (30 ml), ethylene glycol (5 ml) and *p*-toluenesulphonic acid (200 mg) was heated under reflux for 4 hr on a steam bath. The water separating during the reaction was trapped and removed from time to time. The reaction mixture was treated with solid Na_2CO_3 and diluted with ether. The organic layer was washed with water and dried. Removal of solvent furnished XII (3·05 g), b.p. 180° (bath)/0·5 mm. (Found: C, 70·09; H, 9·79. $C_{18}H_{30}O_4$ requires: C, 69·64; H, 9·74%.) The IR spectrum showed bands at: 1727, 1258, 1190, 1156, 1099, 1053, 1000, 945, 917 and 847 cm^{-1}.

3-*Oxo*-12-*diphenyl*-4*β*(H), 5α(H)-*eudesm*-11-*ene* (XIV). Ketal ester (XII; 1·6 g) in dry ether (20 ml) was added to cooled (0°) Grignard reagent prepared from bromobenzene (25 ml), Mg (4 g) and dry ether (30 ml). Subsequently, dry benzene (25 mg) was added and the mixture heated under reflux for 4 hr. It was then cooled and added to cold dil. HCl. The product which was isolated by ether extraction was heated (70°) with acetic acid (70%, 15 ml) for ½ hr. Bromobenzene and diphenyl were removed by steam distillation. The steam-nonvolatile material was extracted with ether, dried and the solvent evaporated. The residue (XIII, 2·28 g) showed bands for a keto group (1698 cm^{-1}) and an hydroxyl group (3472 cm^{-1}). It was dehydrated by heating under reflux for 3 hr with benzene (25 ml) and a small crystal of I_2. The reaction mixture was cooled, diluted with ether and washed with $Na_2S_2O_3$ solution and water. The ether–benzene layer was dried and the solvent distilled off. The residue (1·98 g) was chromatographed on alumina (gr. II, 50 g). Elution with pet. ether–benzene (1:1, 100 ml) furnished the ketone (XIV, 1·30 g) whose IR spectrum did not show absorption for an hydroxyl group. UV spectrum: λ_{max} 245 mμ, log ε 4·09. IR spectrum showed bands at: 1698, 1587, 1481, 1439, 1370, 1175, 1071, 1018, 769, 735 and 699 cm^{-1}. The ketone (XIV) was characterized as the semi-carbazone, m.p. 203–205°, which crystallized from alcohol. (Found: N, 9·57. $C_{28}H_{37}ON_3$ requires: 9·74%.)

Benzylidene derivative (XV). The ketone (XIV; 1·29 g) was dissolved in MeOH (100 ml) and heated under reflux. Benzaldehyde (3·2 g) and subsequently NaOHaq (33%, 20 ml) were added and the mixture kept at 44° in a N_2 atm. for 3 days. Excess benzaldehyde was removed by steam distillation and the steam non-volatile portion extracted with ether and dried. Removal of solvent furnished (1·23 g) of residue which was chromatographed on alumina (gr. II, 50 g). The fraction (897 mg) which was eluted with pet. ether–benzene (1:1, 150 ml) solidified on keeping at 0° for 2 days. Recrystallization from MeOH furnished the benzylidine derivative (XV), m.p. 115–118°. λ_{max} 290 mμ, log ε 4·1 λ_{max} 245, log ε 4·0. (Found: C, 88·33; H, 8·15. $C_{33}H_{38}O$ requires: C, 87·95; H, 8·50%.) The IR spectrum (in nujol) showed bands at: 1672, 1590, 1481, 1370, 1235, 1190, 1124, 1070, 934, 751 and 693 cm^{-1}.

Dimethyl 11-*oxo*-2,3-*seco*-7α(H)-12-*noreudesmane*-2,3-*dioate* (XVII). The benzylidine derivative (XV; 0·800 g) was ozonized in ethyl acetate (25 ml) at 0° for 8 hrs (rate of O_3 formulation 120 mg per hr). To the ozonized solution acetic acid (10 ml) and H_2O_2 (33%, 5 ml) were added and the mixture kept at room temp overnight. The benzoic acid formed was removed by steam distillation and the steam non-volatile material separated into acidic and neutral portions. The acidic portion (0·35 g) was esterified with diazomethane to give XVII (0·300 g), b.p. 180° (bath)/0·3 mm. $(\alpha)_D$ −16° (*c*, 7·5). lit.[15] records $(\alpha)_D$ −20° for the keto ester (XVII). (Found: C, 64·54; H, 8·88. $C_{16}H_{26}O_5$ requires: C, 64·40; H, 8·78%.) The NMR spectrum of XVII is in good agreement with the proposed structure.

Methyl-4-β(H),5α(H) *eudesman*-13-*oate* (XXIII). The semicarbazone, m.p. 172°, of X (0·988 g) was added to a solution of KOH (10 g) in diethylneglycol (30 ml). The mixture was refluxed at 210° in a N_2 atm for 3½ hr and then acidified at 0° and extracted with ether. Removal of solvent and esterification with diazomethane furnished 750 mg of product which was chromatographed on alumina (grade III, 10 g). Elution with pet. ether (60–80°, 100 ml) furnished XXIII (0·45 g), b.p. 170° (bath)/5 mm, $(\alpha)_D$ −4° (*c*, 5·8) (Found: C, 76·65; H, 11·15. $C_{16}H_{28}O_2$ requires: C, 76·14; H, 11·18%.) IR spectrum showed bands at: 3012, 1730, 1466, 1383, 1342, 1258, 1203, 1157, 1060, 938 and 849 cm^{-1}.

11-*Oxo*-4β,5α(H)-12-*noreudesmane* (XXVI). The ester (XXIII, 450 mg) in dry ether (25 ml) was added to a cooled (0°) solution of Grignard reagent prepared from bromobenzene (7 ml), Mg (1 g) and dry ether (50 ml). After completing the addition, the mixture was kept at 0° for ½ hr. Subsequently, dry benzene (25 ml) was added and the mixture heated under reflux for 3 hr, cooled to room temp and poured in cold dil. H_2SO_4 (5%, 50 ml). The product was steam distilled to remove bromobenzene and biphenyl. From the steam non-volatile portion, XXIV (700 mg) was isolated. IR spectrum showed bands at: 3704, 3472, 3040, 2941, 1942, 1880, 1792, 1939, 1672, 1587, 1441, 1439, 1422, 1370, 1149, 1070, 1029, 1005, 909, 740 and 699 cm^{-1}.

To XXIV (700 mg) dissolved in dry pyridine (20 ml) and kept at 0° was added a solution of thionyl chloride (1 ml) in pyridine (5 ml). The mixture was kept at 0° for 45 min and poured onto ice. The product was extracted with ether, washed with cold dil. HCl, Na_2CO_3aq and water and subsequently dried. Evaporation of solvent furnished (0·65 g) of residue which was chromatographed on neutral alumina (grade II, 25 g). The hydrocarbon (XXV; 0·49 g) was eluted with pet. ether (150 ml). The IR spectrum did not exhibit any band in the hydroxyl region. The UV spectrum λ_{max} 243 mμ, log ε 4·05. IR spectrum-bands at: 2941, 1946, 1869, 1802, 1592, 1488, 1439, 1370, 1070, 1020, 740 and 699 cm^{-1}.

The hydrocarbon (XXV, 470 mg) was ozonized at 0° for 3 hr in $CHCl_3$ (rate of O_3 production 120 mg per hr). After removing the solvent at 40° *in vacuo*, the residual ozonide was decomposed by boiling with water for 2 hr. The ozonolysis product (465 mg) was chromatographed on neutral alumina (grade II, 15 g). Elution with ether furnished a mixture of XXVI and benzophenone (0·38 g). IR spectrum bands at: 3030, 1695, 1639, 1587, 1562, 1433 cm^{-1}.

LAH (100 mg) and anhydrous $AlCl_3$ (100 mg) were mixed in dry ether (30 ml) at 0° and kept at room temp for ½ hr. A mixture of benzophenone and XXVI (500 mg) in dry ether (25 ml) was added at room temp and the reaction mixture kept at room temp for 35 min and then treated with water. The product which was isolated by extraction with ether, was chromatographed on neutral alumina (grade II, 15 g). The fraction (0·29 g) eluted with pet. ether was mostly diphenylmethane. The fraction eluted with ether (0·1850 g) was XXVII (IR spectrum showed a prominent band for hydroxyl group at 3390 cm^{-1}). The VPC† indicated that it contained less than 2% impurities.

The alcohol (XXVII, 0·180 g) was oxidized with Jones reagent and the product converted to the semicarbazone which was recrystallized from dil. ethanol. The pure semicarbazone of XXVI melted at 173° (0·12 g). (Found: C, 67·71; H, 9·90. $C_{15}H_{27}ON_3$ requires: C, 67·88; H, 10·26%.)

The ketone (XXVI, 92 mg) was regenerated from its semicarbazone. It had b.p. 165° (bath)/ 3·5 mm, $(\alpha)_D$ −34° (*c*, 1·65). IR spectrum (liquid film), bands at: 2924, 1698, 1451, 1372, 1342, 1267, 1221, 1178 and 1149 cm^{-1}.

Epidihydroeudesmol (XXI). The ketone (XXVI, 80 mg) in dry ether (10 ml) was added dropwise with stirring to a cooled (0°) Grignard reagent prepared from Mg (0·5 g) dry ether (25 ml) and MeI (5 ml). The reaction mixture was then heated to reflux for ½ hr, cooled and decomposed with sat NH_4Claq at 0°. The product (69 mg) which was extracted with ether, on sublimation at 80°/0·5 mm furnished 39 mg of solid m.p. 61–65°, $(\alpha)_D$ −17° (*c*, 3·84). Recrystallization from pet. ether and sublimation furnished XXI, m.p. 80–81° $(\alpha)_D$ −16° (*c*, 0·92) (lit.[16] records m.p. 73–75·5° $(\alpha)_D$ −12·8° for epidihydroeudesmol. IR spectra (in nujol) 3333, 3236, 2941, 1453, 1374, 1269, 1221, 1198, 1183, 1166, 1151, 1136, 1114, 1015, 990, 953, 910 and 853 cm^{-1}. VPC of epidihydroeudesmol exhibited a single peak (retention time 7·9 min) using a polyester column, temp 200°, H_2 as carrier gas. Under similar conditions, XX showed R.T. of (10·5 min), maaliol (5·7 min) and longifolene (1·8 min). (Found: C, 80·91; H, 12·72. $C_{15}H_{28}O$: requires: C, 80·3; H, 12·5%.)

We thank Dr. S. C. Bhattacharyya for his interest in this investigation and Prof. W. Klyne for the optical rotatory dispersion curve of keto ester.

† Taken in the Griffin VPC apparatus MK IIA.
We thank Dr. B. B. Ghatge for the VPC data.