The Constitution and Stereochemistry of Euphol.

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The triterpenoids euphol and lanosterol are similar in many respects. This is illustrated by parallel reactions carried out on rings B and C of the tetracyclic nucleus and by degradations which demonstrate the presence of an *iso*octenyl side chain in both compounds.

Lanostene and euphene are shown to have the same number of methyl groups. In the light of earlier work this demonstrates that ring D of euphol cannot be six-membered.

Dehydrogenation of euphadiene affords 1 : 7 : 8-trimethylphenanthrene; the same degradation applied to *iso*euphadiene gives 1 : 2 : 5-trimethylnaphthalene. This evidence provides strong support for the view that migration of a methyl group is involved in the conversion of euphenol into *iso*euphenol.

A tricyclic diketone from euphenol is shown to have two methylene groupings adjacent to the ketone groups. This observation excludes an earlier formula for euphol.

The constitution and stereochemistry shown in (I; R = OH) are advanced to explain these and earlier observations on the chemistry of euphol.

The triterpenoid alcohol euphol, a major constituent of dried euphorbia latex, was first isolated in a state of purity by Newbold and Spring (*J.*, 1944, 249). In the last decade this compound has been the subject of detailed structural investigation. The present paper summarises new experimental work which, when combined with previous studies cited in detail below, throws considerable light on the constitutional and stereochemical problems involved. Our views on these subjects can be conveniently summarised in the expression (I; R = OH) for euphol. A preliminary communication to this effect has already appeared (Barton, McGhie, Pradhan, and Knight, *Chem. and Ind.*, 1954, 1325).

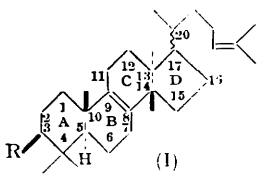
We commence our exposition by reporting work (for preliminary communications see

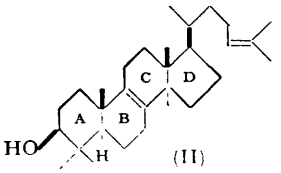
Knight and McGhie, *Chem. and Ind.*, 1953, 920; 1954, 24) which, in agreement with that by others (Christen, Dünnenberger, Roth, Heusser, and Jeger, *Helv. Chim. Acta*, 1952, **35**, 1756, and earlier papers; Barbour, Bennett, and Warren, *J.*, 1951, 2540, and earlier papers; Vilkas, *Ann. Chim.*, 1951, **6**, 325, and earlier papers; Dawson, Halsall, and Swayne, *J.*, 1953, 590), supports a close structural relation between rings A, B, and C of euphol and its side chain and the comparable features of lanosterol (II).

Chromic acid oxidation of euphenyl acetate (III; R = Ac) under mild conditions gives 7-oxoeuphenyl acetate (IV; R = Ac) in poor yield (McDonald, Warren, and Williams, *J.*, 1949, S 155; see Christen *et al.*, *loc. cit.*). This oxidation can be carried out more efficiently with ozone or, alternatively, by treating euphadienyl acetate (V; R = Ac) with performic or perphthalic acid. With the former reagent the unsaturated ketone was formed directly; with the latter a compound, $C_{32}H_{52}O_3$, was isolated which is either an epoxide or the $\beta\gamma$-unsaturated ketone, 7-oxoeuph-9(11)-enyl acetate, for under acid conditions it was smoothly rearranged to the desired (IV; R = Ac). Closely comparable reactions have been reported in the lanosterol series (Birchenough and McGhie, *J.*, 1950, 1249; Cavalla and McGhie, *J.*, 1951, 744; and references there cited).

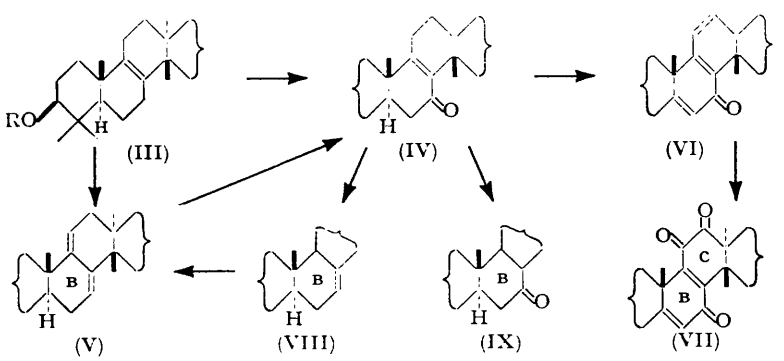
Oxidation of 7-oxoeuphenyl acetate (IV; R = Ac) with selenium dioxide afforded 7-oxoeupha-5 : 8 : 11-trienyl acetate (VI; R = Ac), which was smoothly oxidised by chromic acid to the known diene-trione (VII; R = Ac) (Barbour, Bennett, and Warren, *J.*, 1951, 2540). Both reactions are analogous to transformations of 7-oxolanostenyl acetate already investigated (Cavalla and McGhie, *loc. cit.*).

Wolff–Kishner reduction of 7-oxoeuphenyl acetate (IV; R = Ac) gave, after reacetylation, an isomer of euphenyl acetate, formulated as (VIII; R = Ac), and comparable to lanost-7-enyl acetate which can be obtained by a similar route (Cavalla, McGhie, and Pradhan, *J.*, 1951, 3142; Barton, Fawcett, and Thomas, *ibid.*, p. 3147). On selenium dioxide oxidation, the new isomer (VIII; R = Ac) afforded euphadienyl acetate (V; R = Ac).


(I)


(II)

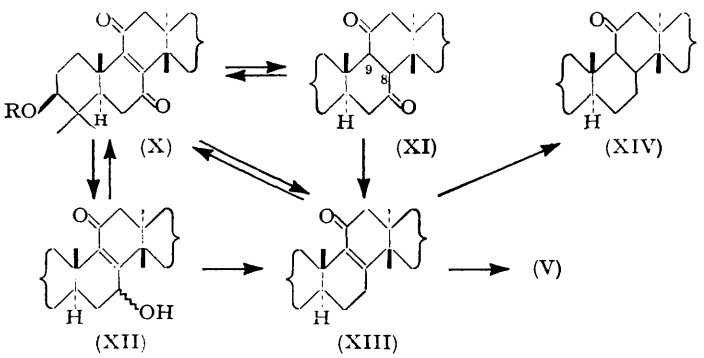
Reduction of 7-oxoeuph-8-enyl acetate (IV; R = Ac) with lithium and liquid ammonia (Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5360, 5366) gave, after reacetylation, 7-oxoeuphanyl acetate (IX; R = Ac). A comparable reduction of 7-oxolanost-8-enyl acetate has already been effected (Barton and Thomas, *Chem. and Ind.*, 1953, 172; *J.*, 1953, 1842). 7-Oxoeuphanyl acetate showed bands (in Nujol) at 1738 (acetate) and 1716 cm.$^{-1}$ (six-ring ketone) in agreement with the assigned constitution.


(III) (IV) (VI) (V) (VIII) (IX) (VII)

Reduction of 7 : 11-dioxoeuphenyl benzoate (X; R = Bz) (Vilkas, Dupont, and Dulou, *Bull. Soc. chim. France*, 1949, 813) with zinc dust and acetic acid furnished the

saturated diketone (XI; R = Bz). The reduction is comparable to that observed in the lanosterol series (Dorée, McGhie, and Kurzer, *J.*, 1949, 988; cf. Christen *et al.*, *loc. cit.*). However, whilst 7 : 11-dioxolanost-8-enyl acetate is reduced to a 1 : 4-dione with *trans*-fusion of rings B and C, the diones in the euphol series appear (cf. Barnes and Barton, *J.*, 1952, 1419) to have the two hydrogen atoms at positions 8 and 9 *cis* to each other (Knight and McGhie, *loc. cit.*). Thus 7 : 11-dioxoeuphanyl acetate (XI; R = Ac) (Christen *et al.*, *loc. cit.*) was easily oxidised back to the parent ene-dione (X; R = Ac) by selenium dioxide. Also alkaline hydrolysis of 7 : 11-dioxoeuphanyl benzoate afforded 7 : 11-dioxoeuphenol (X; R = H), and not the saturated diketone (XI; R = H).

7 : 11-Dioxolanostanyl acetate can easily be obtained from 7 : 11-dioxolanost-8-enyl acetate by catalytic hydrogenation (Dorée, McGhie, and Kurzer, *loc. cit.*) as well as by zinc dust reduction (see above). In contrast, catalytic hydrogenation of 7 : 11-dioxoeuph-8-enyl acetate gives a dihydro-derivative which is still an unsaturated ketone (Haines and Warren, *J.*, 1950, 1562; Barbour and Warren, *Chem. and Ind.*, 1952, 295). Of the various possible formulæ for this compound (Dawson, Halsall, and Swayne, *loc. cit.*), we have established that (XII; R = Ac) is correct. Reduction of 7 : 11-dioxoeuph-8-enyl acetate with sodium borohydride gave a compound identical with that obtained by catalytic hydrogenation. The reduction was also effected, although less conveniently, by the use of aluminium *iso*propoxide in *iso*propanol. Treatment of the monoacetate (XII; R = Ac), which was characterised as the diacetate, with potassium *tert.*-butoxide gave back, after reacetylation, 7 : 11-dioxoeuphenyl acetate (X; R = Ac), no doubt *via* the saturated 7 : 11-diketone (cf. above). Reduction of the monoacetate (XII; R = Ac), or of the derived diacetate, with zinc dust and acetic acid furnished 11-oxoeuph-8-enyl acetate (XIII; R = Ac). The latter was also obtained by Wolff–Kishner reduction of 7 : 11-dioxoeuphenyl acetate (X; R = Ac) or of 7 : 11-dioxoeuphanyl benzoate (XI; R = Bz), followed by acetylation. Oxidation of the monoketone (XIII; R = Ac) with chromic acid gave back the diketone (X; R = Ac), as expected. In agreement with its assigned constitution, the monoketone (XIII; R = Ac) showed an unsaturated six-ring ketone band at 1673 cm.$^{-1}$ in the infra-red (in Nujol). Reduction of this ketone (XIII;



R = Ac) with lithium and liquid ammonia afforded, after reacetylation, 11-oxoeuphanyl acetate, isomeric with the saturated 7-ketone reported above. Reduction of the same ketone (XIII; R = Ac) with sodium and alcohol took a different course and gave, after reacetylation, euphadienyl acetate (V; R = Ac), formed, no doubt, by dehydration of the allylic 11-alcohol.

In our work we had occasion to oxidise euphadienyl benzoate with chromic acid, to give 3β-benzoyloxy-7 : 11-dioxotrisnoreuph-8-enoic acid (cf. Dupont, Dulou, and Vilkas, *Bull. Soc. chim. France*, 1949, 809; Krüsi, *J.*, 1950, 2864; Cavalla, McGhie, Pickering, and Rees, *J.*, 1951, 2474), characterised as the methyl ester. Alkaline hydrolysis gave the known trisnorhydroxy-acid. Reduction of the benzoate acid or of its methyl ester with zinc dust and acetic acid gave the expected dihydro-derivatives. That from the methyl ester was re-oxidised by selenium dioxide to its precursor. Similarly, the methyl

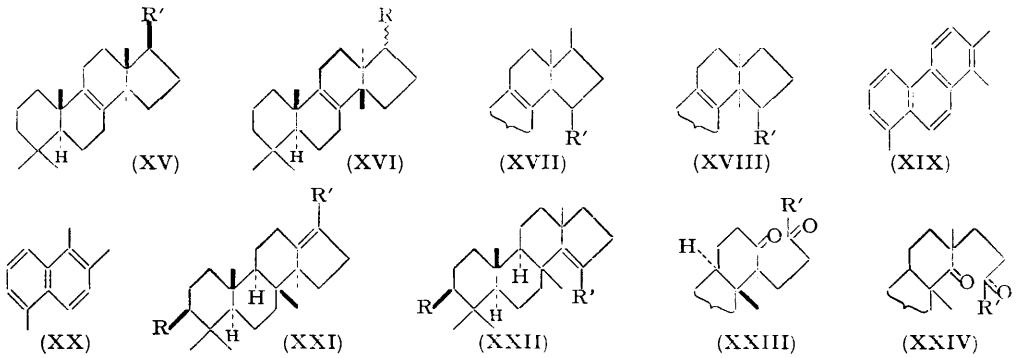
ester of the trisnorhydroxy-acid and its derived acetate were smoothly reduced by zinc dust to the corresponding saturated diketones. Treatment of 3β-hydroxy-7 : 11-dioxotrisnoreuph-8-enoic acid with sodium borohydride afforded the expected 7ξ-hydroxy-compound, reduced by zinc dust to 3β-hydroxy-11-oxotrisnoreuph-8-enoic acid. The latter was also prepared by Wolff–Kishner reduction of the above-mentioned diketo-acid. Selenium dioxide oxidation of the diketo-acid gave the hitherto unknown 3β-hydroxy-7 : 11 : 12-trioxotrisnoreupha-5 : 8-dienoic acid.

The presence of an *iso*octenyl side chain in euphol, identical with that of lanosterol, was established by degradational experiments by Christen, Jeger, and Ruzicka (*Helv. Chim. Acta*, 1951, **34**, 1675). Direct confirmation of this conclusion has been secured (see Knight and McGhie, *loc. cit.*) by vigorous chromic acid oxidation of euphenyl acetate which gave, in small yield, 6-methylheptan-2-one and acetone. Corresponding degradations have been reported on cholesterol (Windaus, *Ber.*, 1913, **46**, 1246; Dirscherl and Nahm, *Annalen*, 1943, **555**, 57) and on lanostenyl acetate (Barton, McGhie, *et al.*, *Chem. and Ind.*, 1951, 1067).

The chemistry of euphol has now reached a position where the nature of rings A, B, and C and of the side chain can be taken as established. The size of ring D as five-membered is implied by experiments of the Zürich group cited by Ruzicka (with Eschenmoser and Heusser, *Experientia*, 1953, **9**, 357). We have shown that ring D is almost certainly *cyclo*pentanic by a quantitative comparison of the infra-red maxima of lanostene (XV; R′ = C_8H_{17}) and euphene (XVI; R′ = C_8H_{17}) in the 1380-cm.$^{-1}$ region of the spectrum (in CCl_4). This region is characteristic for the C–H bending of methyl groups (for example, see Barton, Page, and Warnhoff, *J.*, 1954, 2715, and references there cited). Measured at the same concentration, the curves for lanostene and euphene are identical near 1380 cm.$^{-1}$. This shows that both compounds must have the same number (eight) of methyl groups. With allowances for the fourteen carbon atoms in rings A, B, and C, and the five carbon atoms (other than methyl groups) in the side chain, only three carbon atoms are unplaced with which to construct ring D.

Further evidence that lanostenol and euphenol contain the same number of methyl groups was obtained from Kuhn–Roth *C*-methyl determinations (lanostenol 12·9, euphenol 13·3% of *C*-methyl).

The remaining uncertainties about the constitution of euphol are the position of two methyl groups (now placed at positions 13 and 14) and of the side chain (now placed at position 17). Any satisfactory constitutional proposals must also explain the acid-catalysed



rearrangement of euphenol to *iso*euphenol (Vilkas, Dupont, and Dulou; Christen, Dünnenberger, *et al.*; Dawson, Halsall, and Swayne, *locc. cit.*). Of the formulations that have been considered hitherto for euphol the most pertinent are (XVII; R′ = C_8H_{15}) (Christen *et al.*, *loc. cit.*) and (XVIII; R′ = C_8H_{15}) (Ruzicka, *loc. cit.*). The possibility that euphol could be 14-*iso*lanosterol has also been mentioned in passing (Ruzicka, *loc. cit.*).

We consider first the nature of the *iso*euphenol rearrangement. This could involve either the movement of the ethylenic linkage (cf. the isomerisation of Δ^8- to Δ^{14}-stenols) or migration of the methyl groups induced by formation of a carbonium ion. Now

dehydrogenation of lanostene affords 1 : 2 : 8-trimethylphenanthrene (XIX) (Barton, Fawcett, and Thomas, *J.*, 1951, 3147; Voser, Mijovic, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1951, **34**, 1585), the two adjacent methyl groups corresponding to those attached originally at $C_{(13)}$ and $C_{(14)}$. Comparable dehydrogenation of euphadiene (I; R = H) (cf. unpublished work mentioned by Christen *et al.*, *loc. cit.*; McDonald, Warren, and Williams, *J.*, 1949, S 155) also afforded 1 : 2 : 8-trimethylphenanthrene as sole isolatable product. In contrast, dehydrogenation of *iso*euphadiene, prepared from euphadiene (I; R = H) by acid-catalysed rearrangement in the usual way, gave 1 : 2 : 5-trimethylnaphthalene (XX). In spite of careful fractionation no 1 : 2 : 8-trimethylphenanthrene could be detected. That the side-chain *iso*propylidene group of euphadiene was not complicating the course of the rearrangement was shown by ozonolysis of *iso*euphadiene which gave the expected acetone.

The simplest interpretation of these critical experiments is that methyl groups are attached at positions 13 and 14 in euphadiene and that conversion into *iso*euphadiene involves migration of a methyl group from position 14 to position 8. There are then two possible expressions for *iso*euphadiene, namely (XXI; R = H, R′ = C_8H_{15}), which results from the migration of two methyl groups, and (XXII; R = H, R′ = C_8H_{15}) whose formation involves migration of only one methyl group.

In support of the attachment of two methyl groups at positions 13 and 14, we have shown that 7 : 11 : 12-trioxoeupha-5 : 8-dienyl acetate cannot be brominated even under vigorous conditions. This is in agreement with the absence of hydrogen from position 14.

Christen *et al.* (*loc. cit.*) have already shown that ozonolysis of *iso*euphenyl acetate affords a crystalline diketone. On the basis of (XXI or XXII; R = OAc, R′ = C_8H_{17}) for *iso*euphenyl acetate the diketone must be (XXIII or XXIV respectively; R = OAc, R′ = C_8H_{17}). We have accumulated decisive evidence in favour of (XXIII; R = OAc, R′ = C_8H_{17}) for the diketone and thus of (XXI; R = OAc, R′ = C_8H_{17}) for *iso*euphenyl acetate. The diketone forms a dioxime (Christen *et al.*, *loc. cit.*). It would be unexpected if a compound such as (XXIV; R = OAc, R′ = C_8H_{17}) furnished more than a monoxime. The formation of a dioxime from (XXIII; R = OAc, R′ = C_8H_{17}) would, however, be acceptable (cf., for discussion, Barton, *J.*, 1953, 1027). The diketone in question consumes five mols. on titration with bromine (see Table), thus indicating at least five replaceable

Compound	No. of α-hydrogen	Uptake of Br (mols.) *				
Time (days):		1	2	3	4	5
Cholestan-3-one	4	2·72	3·56	3·74	3·89	4·01
Diketone (XXIII; R = OAc, R′ = C_8H_{17})	5	4·52	4·75	4·94	5·00	5·05
Lanostane-3 : 7-dione †	6	2·78	3·09	3·28	3·37	3·42

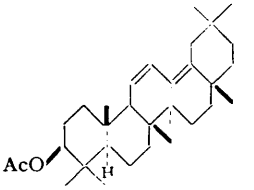
* Brominations were carried out at 37° as detailed on p. 886.
† Dorée, McGhie, and Kurzer, *J.*, 1948, 988.

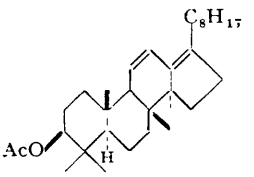
α-hydrogen atoms. A compound (XXIV; R = OAc, R′ = C_8H_{17}) would, of course, consume only up to three mols. of bromine, whereas (XXIII; R = OAc, R′ = C_8H_{17}) has exactly the five replaceable α-hydrogen atoms required. That the bromination was not complicated by a further rearrangement was shown by reducing the total bromination product with zinc dust back to the initial diketone.

Furthermore a study of the infra-red spectrum (in CCl_4) of the hydroxy-diketone (XXIII or XXIV; R = OH, R′ = C_8H_{17}) revealed a band at 1412 cm.$^{-1}$ characteristic of CH_2 groups adjacent to C=O. The intensity of this band was determined (cf. Barnes, Barton, Cole, Fawcett, and Thomas, *J.*, 1953, 571, and references there cited) quantitatively relative to the corresponding band (at 1420 cm.$^{-1}$) due to two CH_2·CO groups in α-amyrane-3 : 12-dione (kindly supplied by Mr. K. H. Overton). In this way it was shown that there must be two ·CH_2·CO groups in the hydroxy-ketone, which must be formulated, therefore, as (XXIII; R = OH, R′ = C_8H_{17}).

The new constitution (XXI; R = OAc, R′ = C_8H_{17}) for *iso*euphenyl acetate must also, of course, permit the formulation of *iso*euphadienyl acetate (Vilkas, *Bull. Soc. chim. France*, 1950, 582; *Ann. Chim.*, 1951, **6**, 325), the conjugated diene obtained by acid-catalysed dehydration of *iso*euphenyl acetate oxide. The ultra-violet absorption spectrum

of *iso*euphadienyl acetate with its triple peak is very similar to that of olea-11 : 13(18)-dienyl acetate (XXV) (Ruzicka, Müller, and Schellenberg, *Helv. Chim. Acta*, 1939, **22**, 767; Barton and Brooks, *J.*, 1951, 257). A probable structure for *iso*euphadienyl acetate is, therefore, (XXVI). In agreement with this formula the infra-red spectra of olea-11 : 13(18)-dienyl

(XXV) 



(XXVI)

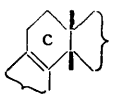
acetate and of *iso*euphadienyl acetate (in CS_2) were almost identical in the 700—800-cm.$^{-1}$ region. Olea-11 : 13(18)-dienyl acetate showed bands at 729, 759, and 778 cm.$^{-1}$ and *iso*euphadienyl acetate showed bands at 731, 755, and 772 cm.$^{-1}$, both spectra indicating the grouping *cis*-CH:CH· in a six-membered ring (see Henbest, Meakins, and Wood, *J.*, 1954, 800). Evidence against the formulation (XXVI) for *iso*euphadienyl acetate was, apparently, offered by the findings of Vilkas (*loc. cit.*) that catalytic hydrogenation gave "γ-euphenyl acetate." Olea-11 : 13(18)-dienyl acetate is, of course, readily hydrogenated to olean-13(18)-enyl acetate. A repetition of Vilkas's experiment (*loc. cit.*) (cf. Christen *et al.*, *loc. cit.*) gave back *iso*euphenyl acetate and not "γ-euphenyl acetate." It will be recalled that olea-11 : 13(18)-dienyl acetate is prepared by the selenium dioxide oxidation of β-amyrin acetate (olean-12-enyl acetate). Similar oxidation of *iso*euphenyl acetate gave *iso*euphadienyl acetate. The formula (XXVI) appears from all this evidence to be well supported.

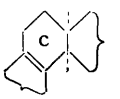
The stereochemistry assigned to the methyl groups at positions 13 and 14 in (I; R = OH) for euphol is based on the following considerations. First, this stereochemistry forces the molecule to assume in rings B and C the unfavourable conformation of two half-boats. We believe that this steric strain provides a *conformational driving force* for methyl-group migration, to give the *iso*euphenol stereochemistry, where all three six-membered rings can adopt the favourable chair conformations. The methyl groups in lanostenol do not, of course, migrate when a carbonium ion is formed at position 8, as in the equilibration of lanost-8- and -7-enyl acetate. There is however no reason why the methyl group at position 14 should move to position 8 since the change would be from a favourable all-chair (or half-chair if one considers the *cyclo*hexene rings) conformation to a relatively unfavourable conformation. We are of the opinion that more attention should be paid to conformational effects of this type in considering the likely incidence of carbonium-ion rearrangements in alicyclic systems.

Secondly, the abnormal hydrogenation of 7 : 11-dioxoeuphenyl acetate (see above) is readily explained with the aid of models based on the stereochemistry indicated for positions 13 and 14.

Thirdly, the placing of the $C_{(13)}$- and $C_{(14)}$-methyl groups *trans* to each other is mechanistically desirable if the two migrations are to be concerted.

Fourthly, the two further arrangements (XXVII) and (XXVIII) for the stereochemistry can be shown to be improbable. Thus, the structure (XXVII) could hardly explain the

(XXVII) 



(XXVIII)

failure (Christen *et al.*, *loc. cit.*) of euphenyl acetate to react with osmium tetroxide under conditions where Δ^8-stenols react readily (Barton and Cox, *J.*, 1949, 214; Djerassi, Yashin, and Rosenkranz, *J. Amer. Chem. Soc.*, 1952, **74**, 422) and the nuclear double bond of lanosterol is untouched (Wieland and Benend, *Z. physiol. Chem.*, 1942, **274**, 215). The stereochemistry of (XXVIII) would not be compatible with the marked steric hindrance shown by the 11-oxo-grouping in the appropriate euphol derivatives (see above).

The configurations assigned to ring A have already been discussed (cf. Christen *et al.*, *loc. cit.*) adequately in our preliminary communication (Barton, McGhie, Pradhan, and Knight, *loc. cit.*) and need not be repeated here. Our tentative assignments of configuration at $C_{(17)}$ and $C_{(20)}$ made in the same article were based on molecular-rotation considerations. Professor L. Ruzicka and Dr. O. Jeger of Zürich have been kind enough to inform us of new evidence (Arigoni, Viterbo, Dünnenberger, Jeger, and Ruzicka, *Helv. Chim. Acta*, in the press) that shows the configuration at $C_{(20)}$ to be the same as that in lanosterol and thus disproves our earlier views. At the same time they have communicated to us details of additional experiments which support the formula (I; R = OH) for euphol. Although Arigoni *et al.* (*loc. cit.*) favour an α-configuration at $C_{(17)}$ for the side chain, on the basis of a totally concerted mechanism for the *iso*euphenol rearrangement, we believe that, if molecular-rotation considerations cannot be applied, then the non-committal symbol of (I; R = OH) is all that is justified at the present time. Dr. T. G. Halsall has also kindly informed us of unpublished experiments, carried out at Manchester, on the chromic acid oxidation of *iso*euphenyl acetate. The results obtained are incompatible with the earlier formulæ for this acetate, but can be interpreted in terms of (XXI; R = OAc, R′ = C_8H_{17}) (see above).

Experimental

Rotations are for $CHCl_3$ solutions unless stated otherwise; ultra-violet absorption spectra were taken in ethanol on the Unicam S.P. 500 Spectrophotometer. Infra-red spectra were kindly determined by Mr. D. Orr of the Chester Beatty Research Institute and by Messrs. Glaxo Laboratories Ltd.

Light petroleum refers to the fraction of b. p. 60—80° unless specified to the contrary.

7-Oxoeuph-8-enyl Acetate.—(*a*) Eupha-7 : 9(11)-dienyl acetate (Vilkas, *Bull. Soc. chim. France*, 1950, 582; Barbour, Bennett, and Warren, *J.*, 1951, 2540) (500 mg.) in chloroform (2·5 ml.) and formic acid (99—100%; 25 ml.) was heated to 60° and to the well-stirred solution hydrogen peroxide (30%; 1 ml.) was added. The stirred mixture was allowed to cool to room temperature (2 hr.). Chromatography over alumina (12 × 1 cm.) and elution with benzene–light petroleum gave 7-oxoeuph-8-enyl acetate (50 mg.), m. p. (from aqueous methanol) 162—164°.

(*b*) Euphenyl acetate (1·0 g.) in ethyl acetate (25 ml.) was ozonised (4% ozone) at −5° for 2 hr. After being washed with ferrous sulphate solution, the ethyl acetate was removed *in vacuo* and the product chromatographed over alumina (12 × 1 cm.). Elution with 7 : 1 benzene–light petroleum gave 7-oxoeuph-8-enyl acetate (170 mg.), m. p. (from aqueous methanol) 169—170°, $[\alpha]_D$ +35° (*c*, 0·90), $\lambda_{max.}$ 255 mμ (log ε 4·05) (Found: C, 79·0; H, 10·8. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%).

(*c*) Eupha-7 : 9(11)-dienyl acetate (500 mg.) was treated with ethereal perphthalic acid (1·5 mols.) at room temperature for 7 days. The product was chromatographed over alumina (7 × 1 cm.), elution being with benzene–light petroleum. Crystallisation from methanol gave a *compound* (240 mg.), m. p. 119—120°, $[\alpha]_D$ −4° (*c*, 0·3) (Found: C, 78·8; H, 10·55. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). This compound (500 mg.) in acetic acid (15 ml.) was treated with concentrated sulphuric acid (2 drops) under reflux for 10 min. Crystallisation of the product from aqueous methanol afforded 7-oxoeuph-8-enyl acetate (300 mg.), m. p. and mixed m. p. 167—169°, $[\alpha]_D$ +33° (*c*, 0·3), $\lambda_{max.}$ 255 mμ (log ε 3·96).

Dehydrogenation of 7-Oxoeuph-8-enyl Acetate with Selenium Dioxide.—7-Oxoeuph-8-enyl acetate (88·5 mg.) in acetic acid (10 ml.) with selenium dioxide (60 mg.) was heated under reflux for 3 hr. Crystallisation of the product from aqueous methanol gave *7-oxoeupha-5 : 8 : 11-trienyl acetate* (50 mg.) as small plates, m. p. 188—189°, $[\alpha]_D$ −12° (*c*, 0·2), $\lambda_{max.}$ 256 and 327 mμ (log ε 3·9 and 3·9) (Found: C, 79·8; H, 10·0 $C_{32}H_{48}O_3$ requires C, 80·0; H, 10·1%)

This trienone (27 mg.) in acetic acid (5 ml.) was treated at room temperature with chromic acid (27 mg.) in acetic acid (5 ml.). The mixture was then kept at 60—65° for 90 min. Crystallisation from methanol gave 7 : 11 : 12-trioxoeupha-5 : 8-dienyl acetate, m. p. 184—185°, $[\alpha]_D$ −18° (*c*, 0·1), $\lambda_{max.}$ 283 mμ (log ε 3·85), undepressed in m. p. on admixture with an authentic specimen (Barbour, Bennett, and Warren, *J.*, 1951, 2540) of m. p. 189—191°, $[\alpha]_D$ −19° (*c*, 0·6), $\lambda_{max.}$ 284 mμ (log ε 3·9).

Euph-7-enyl Acetate.—7-Oxoeuph-8-enyl acetate (see above) (290 mg.), hydrazine hydrate (100%; 0·4 ml.), and diethylene glycol (12 ml.) were heated at 185° for 1 hr., then cooled to

70°. A solution of sodium (300 mg.) in diethylene glycol (5 ml.) was added, the mixture reheated to 210—220°, and water removed by distillation. After 5 hr. at 210—220°, the product was extracted in the usual way and reacetylated by pyridine (2 ml.) and acetic anhydride (5 ml.) on the steam-bath. Chromatography over alumina (6 × 1 cm.) and elution with light petroleum gave euph-7-enyl acetate, m. p. (from methanol–ethanol) 92—94°, $[\alpha]_D$ −60° (*c*, 0·5) (Found: C, 81·3; H, 11·8. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). Oxidation of this compound (50 mg.) in acetic acid (7 ml.) with selenium dioxide (30 mg.) under reflux for 3 hr., followed by chromatography of the product over alumina (5 × 0·5 cm.) and elution with light petroleum, gave eupha-7 : 9(11)-dienyl acetate, m. p. 109—110°, $[\alpha]_D$ −75° (*c*, 0·2), $\lambda_{max.}$ 232, 239, and 248 mμ (log ε 4·2, 4·3, and 4·15 respectively), undepressed in m. p. on admixture with an authentic specimen (Vilkas, *loc. cit.*) of m. p. 112—113°, $[\alpha]_D$ −80° (*c*, 0·5), $\lambda_{max.}$ 232, 239, and 247 mμ (log ε 4·15, 4·24, and 4·0) (Found: C, 81·9; H, 11·2. Calc. for $C_{32}H_{50}O_2$: C, 82·0; H, 11·2%).

7-Oxoeuphanyl Acetate.—Lithium (30 mg.) was dissolved in dry liquid ammonia (40 ml.), and 7-oxoeuph-8-enyl acetate (200 mg.) in ether (4 ml.) was added. After 10 min. the excess of lithium was destroyed by the addition of 1 : 1 *tert.*-butanol–ether (5 ml.). The product was reacetylated with pyridine–acetic anhydride, and the resultant acetate chromatographed over alumina (7 × 0·5 cm.). Elution with benzene gave *7-oxoeuphanyl acetate* (40 mg.), m. p. (from methanol) 116—117°, $[\alpha]_D$ −72° (*c*, 0·4) (Found: C, 79·1; H, 11·0. $C_{32}H_{54}O_3$ requires C, 78·9; H, 11·2%).

7 : 11-Dioxoeuphanyl Benzoate.—7 : 11-Dioxoeuphenyl benzoate {m. p. 186—187°, $[\alpha]_D$ +54° (*c*, 1·10), $\lambda_{max.}$ 272 mμ (log ε 4·12)} (Vilkas, Dupont, and Dulou, *Bull. Soc. chim. France*, 1949, 813) (1·0 g.) in hot acetic acid (20 ml.) was treated under reflux with zinc dust (2·0 g.) added portionwise during 15 min. Crystallisation of the product from methanol gave *7 : 11-dioxoeuphanyl benzoate*, m. p. 176—177°, $[\alpha]_D$ −90° (*c*, 0·4) (Found: C, 78·7; H, 10·0. $C_{37}H_{54}O_4$ requires C, 78·9; H, 9·8%). Similar reduction of 7 : 11-dioxoeuphanol and its acetate afforded 7 : 11-dioxoeuphanol and its acetate respectively (Christen *et al.*, *Helv. Chim. Acta*, 1952, **35**, 1756). 7 : 11-Dioxoeuphanyl benzoate (700 mg.) was hydrolysed with alcoholic potassium hydroxide under reflux for 3 hr. Crystallisation from aqueous methanol gave 7 : 11-dioxoeuph-8-enol, m. p. 118—119°, $[\alpha]_D$ +25° (*c*, 0·3), $\lambda_{max.}$ 272 mμ (log ε 3·9), identical with a specimen, m. p. 119—120°, $[\alpha]_D$ +26° (*c*, 0·3), obtained in the same way from 7 : 11-dioxoeuphenyl acetate.

7 : 11-Dioxoeuphanyl acetate (500 mg.) in acetic acid (20 ml.) was refluxed with selenium dioxide (250 mg.), dissolved in a minimum of water, for 90 min. Chromatography of the product over alumina (10 × 1 cm.), elution with light petroleum, and crystallisation from methanol gave 7 : 11-dioxoeuph-8-enyl acetate, identified by m. p., mixed m. p., rotation, and absorption spectrum.

Wolff–Kishner Reduction of 7 : 11-Dioxoeuph-8-enyl Acetate.—The diketone (3·0 g.) in diethylene glycol (150 ml.) and hydrazine hydrate (100%; 3 ml.) was heated for 1 hr. at 185—190°, then cooled to 70°. Sodium (3·0 g.), dissolved in diethylene glycol (30 ml.), was added and the mixture refluxed at 220° for 6 hr. The product was acetylated with pyridine (5 ml.) and acetic anhydride (10 ml.) overnight at room temperature and then chromatographed over alumina (15 × 1 g.). Elution with light petroleum (500 ml.) and with benzene–light petroleum (800 ml.) gave *11-oxoeuph-8-enyl acetate* (1·5 g.), m. p. (from methanol) 130—131°, $[\alpha]_D$ +28° (*c*, 0·4), $\lambda_{max.}$ 255 mμ (log ε 3·99) (Found: C, 79·6; H, 10·8. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). Wolff–Kishner reduction of 7 : 11-dioxoeuphanyl benzoate (see above) likewise afforded 11-oxoeuph-8-enyl acetate, identical (m. p., mixed m. p., rotation, and absorption spectrum) with the material described above.

Reduction of 11-oxoeuph-8-enyl acetate (200 mg.) in *iso*propanol (20 ml) with sodium under reflux until saturated and heating the product with pyridine (2 ml.) and acetic anhydride (5 ml.) on the water-bath for 2 hr. gave eupha-7 : 9(11)-dienyl acetate, identified by m. p., mixed m. p., rotation, and absorption spectrum.

11-Oxoeuph-8-enyl acetate (100 mg.) in acetic acid (5 ml.) was treated with chromic acid (100 mg.) in acetic acid (90%; 5 ml.) at 50° for 1 hr. Chromatography over alumina, elution with light petroleum, and crystallisation from methanol furnished 7 : 11-dioxoeuph-8-enyl acetate, identified by m. p., mixed m. p., rotation, and absorption spectrum.

11-Oxoeuphanyl Acetate.—To a stirred solution of lithium (10 mg.) in liquid ammonia (25 ml.), 11-oxoeuph-8-enyl acetate (500 mg.) in dry ether (5 ml.) and small pieces of metallic lithium (40 mg.) were added at such a rate that the initial blue colour was just maintained. After completion of the addition the mixture was stirred for a further 10 min. before adding ammonium chloride (4 g.) and allowing the whole to warm to room temperature. Acetylation

of the product with pyridine (3 ml.) and acetic anhydride (10 ml.) for 2 hr. on the water bath, chromatography over alumina (6 × 0·5 cm.), and elution with 4 : 1 light petroleum–benzene gave 11-*oxoeuphanyl acetate*, m. p. (from methanol) 140—141°, $[\alpha]_D$ −51° (*c*, 0·3) (Found: C, 78·6; H, 11·0. $C_{32}H_{54}O_3$ requires C, 78·9; H, 11·2%).

Reduction of 7 : 11-*Dioxoeuph*-8-*enyl Acetate with Sodium Borohydride*.—The diketone (1·0 g.) in methanol (40 ml.) was treated with sodium borohydride (700 mg.) in methanol (10 ml.) at room temperature for 24 hr. Crystallisation from aqueous methanol afforded 7ξ-*hydroxy*-11-*oxoeuph*-8-*enyl acetate*, m. p. 204—205°, $[\alpha]_D$ −3° (*c*, 0·7), $\lambda_{max.}$ 257 mμ (log ε 3·9) (Found: C, 76·7; H, 10·6. $C_{32}H_{52}O_4$ requires C, 76·7; H, 10·5%). Acetylation with pyridine (2 ml.) and acetic anhydride (8 ml.) at room temperature for 14 hr. gave the *diacetate*, m. p. (from methanol) 127—128°, $[\alpha]_D$ ±0° (*c*, 0·2), $\lambda_{max.}$ 257 mμ (log ε 3·9) (Found: C, 75·0; H, 9·8. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%). The hydroxy-acetate was identical [m. p., mixed m. p., rotation, absorption spectrum, and analysis (Found: C, 76·6; H, 10·35%)] with the compound obtained earlier by Barbour and Warren (*Chem. and Ind.*, 1952, 295) by catalytic hydrogenation of 7 : 11-dioxoeuphenyl acetate.

The diacetate (see above) was also obtained as follows. 7 : 11-Dioxoeuph-8-enyl acetate (1·0 g.) in dioxan (10 ml.) with aluminium *iso*propoxide (6·0 g.) in *iso*propanol (25 ml.) was heated under reflux for 1 hr. The *iso*propanol was then slowly distilled off until no more acetone was evolved (2 : 4-dinitrophenylhydrazine). The refluxing was then repeated for 1 hr., being followed by distillation. This was repeated 14 times, dry *iso*propanol being added after each distillation to maintain a constant volume. Acetylation with pyridine and acetic anhydride, chromatography over alumina (12 × 1 cm.), and elution with 1 : 2 benzene–light petroleum gave the diacetate, identified by m. p., mixed m. p., rotation, and absorption spectrum.

7ξ-Hydroxy-11-oxoeuph-8-enyl acetate (500 mg.) in acetic acid–acetic anhydride (1 : 1; 80 ml.) was heated under reflux for 15 min. with zinc dust (3·0 g.). The product crystallised readily from methanol, to give 11-oxoeuph-8-enyl acetate (300 mg.) identified by m. p., mixed m. p., rotation, absorption spectrum, and analysis (Found: C, 79·1; H, 10·7. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). Similar reduction of the analogous diacetate (see above) also afforded 11-oxoeuph-8-enyl acetate, identified as indicated above.

7ξ-Hydroxy-11-oxoeuph-8-enyl acetate (500 mg.) in *tert.*-butanol (40 ml.) containing potassium (570 mg.) was heated under reflux for 1 hr. The product was acetylated with pyridine (3 ml.) and acetic anhydride (15 ml.) on the steam-bath for 2 hr. Chromatography over alumina, elution with light petroleum, and crystallisation from methanol afforded 7 : 11-dioxoeuph-8-enyl acetate (150 mg.), identified by m. p., mixed m. p., rotation, and absorption spectrum.

Attempted Bromination of 7 : 11 : 12-*Trioxoeupha*-5 : 8-*dienyl Acetate*.—The diene-trione (Barbour, Bennett, and Warren, *J.*, 1951, 2540) (250 mg.) in acetic acid (10 ml.) was treated in the cold with a solution of bromine (1 ml.; 3% v/v) in acetic acid and 48% hydrobromic acid–acetic acid (one drop) and then heated for 1 hr. at 80°. The product was identified as unchanged starting material by m. p., mixed m. p., rotation, and absorption spectrum. The same result was observed after 90 minutes' heating at 100°.

Chromic Acid Oxidation of Euphadienyl Benzoate.—The benzoate (10 g.) in acetic acid (1 l.) at 55° was treated with chromic acid (20 g.) in acetic acid (90%; 150 ml.) added with stirring during 1 hr. The stirring was continued for a further 90 min. The solution was poured into dilute sulphurous acid, and the yellow precipitate was collected, dissolved in ether, and extracted with dilute potassium hydroxide solution. The acid thus extracted was recovered in the usual way and crystallised from aqueous acetone or from methanol, to give 3β-*benzoyloxy*-7 : 11-*dioxotrisnoreuph*-8-*enoic acid*, m. p. 202—203°, $[\alpha]_D$ +44° (*c*, 0·5), $\lambda_{max.}$ 272 mμ (log ε 4·1) (Found: C, 74·5; H, 8·7. $C_{34}H_{44}O_6$ requires C, 74·5; H, 8·4%). The *methyl ester*, prepared with diazomethane, had m. p. 164—165°, $[\alpha]_D$ +44° (*c*, 0·5) (Found: C, 74·9; H, 8·3. $C_{35}H_{46}O_6$ requires C, 74·7; H, 8·3%). Similar oxidation of euphadienyl acetate gave an acid fraction which on methylation afforded the known (Krüsi, *J.*, 1950, 2864; Bennett, Krüsi, and Warren, *J.*, 1951, 2534) acetate methyl ester (Found: C, 71·7; H, 8·8. Calc. for $C_{30}H_{44}O_6$: C, 71·9; H, 8·9%).

Methyl 3β-benzoyloxy-7 : 11-dioxotrisnoreuph-8-enoate (4·0 g.) in acetic acid (100 ml.) was treated under reflux with zinc dust (10 g.) added portionwise during 15 min. After a further 20 minutes' refluxing the product, isolated in the usual way, crystallised from chloroform–methanol to give *methyl* 3β-*benzoyloxy*-7 : 11-*dioxotrisnoreuphanoate*, m. p. 191—192°, $[\alpha]_D$ −98° (*c*, 0·4) (Found: C, 74·8; H, 8·6. $C_{35}H_{48}O_6$ requires C, 74·5; H, 8·5%). Dehydrogenation

of this compound with selenium dioxide as described above for 7 : 11-dioxoeuphanyl acetate gave back methyl 3β-benzoyloxy-7 : 11-dioxotrisnoreuph-8-enoate.

The trisnor-acid benzoate (see above) (7·0 g.) in methanol (25 ml.) was treated with ethanolic potassium hydroxide (7%; 300 ml.) under reflux for 3 hr. Crystallisation from ethyl acetate gave 3β-hydroxy-7 : 11-dioxotrisnoreuph-8-enoic acid (Dupont, Dulou, and Vilkas, *Bull. Soc. chim. France*, 1949, 809) (4·0 g.), m. p. 232—233°, $[\alpha]_D$ −9° (*c*, 0·7 in pyridine), $\lambda_{max.}$ 271 mμ (ε 9500).

Zinc dust reduction of methyl 3β-hydroxy-7 : 11-dioxotrisnoreuph-8-enoate as for the benzoate methyl ester (see above) gave the corresponding saturated *diketone*, m. p. 166—168°, $[\alpha]_D$ −142° (*c*, 0·9) (Found : C, 73·2; H, 9·8. $C_{28}H_{44}O_5$ requires C, 73·0; H, 9·7%). The corresponding *acetate methyl ester*, prepared similarly, had m. p. 216—218°, $[\alpha]_D$ −116° (*c*, 0·4) (Found : C, 71·2; H, 9·1. $C_{30}H_{46}O_6$ requires C, 71·7; H, 9·3%). The corresponding *benzoate acid* had m. p. 195—197°, $[\alpha]_D$ −100° (*c*, 0·2) (Found : C, 73·0; H, 8·6. $C_{34}H_{46}O_6$ requires C, 73·2; H, 8·4%).

3β : 7ξ-*Dihydroxy*-11-*oxotrisnoreuph*-8-*enoic Acid*.—The 7 : 11-dioxo-acid (see above) (500 mg.) in methanol (25 ml.) was treated with sodium borohydride (400 mg.) in methanol (15 ml.) for 24 hr. at room temperature. Crystallisation of the product from aqueous methanol afforded 3β : 7ξ-*dihydroxy*-11-*oxotrisnoreuph*-8-*enoic acid*, m. p. 232—233°, $[\alpha]_D$ −44° (*c*, 0·7 in pyridine), $\lambda_{max.}$ 257 mμ (log ε 3·85) (Found : C, 72·4; H, 9·3. $C_{27}H_{42}O_5$ requires C, 72·6; H, 9·5%). The acid (130 mg.) and zinc dust (500 mg.) in acetic acid (15 ml.) were heated on the steam-bath for 2 hr. Crystallisation of the product from aqueous acetone gave 3β-*hydroxy*-11-*oxotrisnoreuph*-8-*enoic acid*, m. p. 224—226°, $\lambda_{max.}$ 256 mμ (log ε 3·8) (Found : C, 75·6; H, 10·1. $C_{27}H_{42}O_4$ requires C, 75·3; H, 9·85%). This acid was also prepared by Wolff–Kishner reduction as detailed for the analogous 7 : 11-dioxoeuph-8-enyl acetate (see above).

Selenium Dioxide Oxidation of 3β-*Hydroxy*-7 : 11-*dioxotrisnoreuph*-8-*enoic Acid*.—The acid (650 mg.), selenium dioxide (450 mg.), and dioxan (15 ml.) were heated together in a sealed tube at 180° for 4 hr. Crystallisation of the product from aqueous acetone (charcoal) gave 3β-*hydroxy*-7 : 11 : 12-*trioxotrisnoreupha*-5 : 8-*dienoic acid* (250 mg.), m. p. 202—203°, $[\alpha]_D$ −20° (*c*, 0·4), $\lambda_{max.}$ 285 mμ (log ε 3·85) (Found : C, 71·4; H, 7·8. $C_{27}H_{36}O_6$ requires C, 71·0; H 7·95%).

Isolation of 6-*Methylheptan*-2-*one*.—Euphenyl acetate (20 g.) in acetic acid (160 ml.) was heated to boiling in a distillation-flask fitted with condenser, receiver, and dropping funnel. To the boiling mixture chromic acid (60 g.) in acetic acid (80%; 180 ml.) and potassium persulphate (14 g.) in water (100 ml.) were added slowly during 1 hr. The rate of distillation was made equal to the rate of addition. When the addition was complete, aqueous acetic acid (1 : 1; 150 ml.) was added and the equivalent volume distilled off. The combined distillates were neutralised (30% aqueous sodium hydroxide) and the mixture was steam-distilled. The first 100 ml. of distillate were treated with excess of 2 : 4-dinitrophenylhydrazine hydrochloride solution and left at 0° overnight. The precipitate was collected and chromatographed over alumina to give 6-methylheptan-2-one 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 77—78°, $\lambda_{max.}$ 366 mμ (log ε 4·36) (Found : C, 54·4; H, 6·4; N, 18·1. Calc. for $C_{14}H_{20}O_4N_4$: C, 54·5; H, 6·6; N, 18·2%). Subsequent eluates contained acetone 2 : 4-dinitrophenylhydrazone, identified by m. p. and mixed m. p.

Dehydrogenation of Euphadiene.—Euphadiene (Roth and Jeger, *Helv. Chim. Acta*, 1949, **32**, 1620; Vilkas, Dupont, and Dulou, *Bull. Soc. chim. France*, 1949, 813; Vilkas, *Ann. Chim.*, 1951, **6**, 325) (19 g.) and selenium powder (38 g.) were heated together at 350° for 48 hr. After cooling, the black residue was ground and extracted under reflux with light petroleum (250 ml.) for 3 hr. After filtration the light petroleum extract was chromatographed over alumina (25 × 2 cm.). Elution with light petroleum (3 × 300 ml.) gave a solid which crystallised from alcohol to give a product, m. p. 105—115°. This was rechromatographed over alumina; elution with light petroleum gave crude 1 : 7 : 8-trimethylphenanthrene (650 mg.) of m. p. 130—136°. Conversion into the picrate gave (from alcohol) 1 : 7 : 8-trimethylphenanthrene picrate (450 mg.), identified by m. p., mixed m. p., and analysis (Found : C, 61·6; H, 4·1; N, 9·7. Calc. for $C_{23}H_{19}O_7N_3$: C, 61·45; H, 4·25; N, 9·35%). The picrate was reconverted into 1 : 7 : 8-trimethylphenanthrene which was identified by m. p. and mixed m. p. (145—146°), ultra-violet absorption spectrum ($\lambda_{max.}$ 215, 226, 254, 262, 283, 294, and 306 mμ; ε 35,100, 18,500, 44,000, 57,000, 12,500, 12,800, and 15,700) and analysis (Found : C, 92·5; H, 7·3. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%).

iso*Euphadiene*.—Euphadiene (2·0 g.) in glacial acetic acid (75 ml.) containing aqueous 2N-sulphuric acid (2 ml.) was refluxed for 2 hr. The product, in light petroleum, was filtered

over alumina (50 g.). Elution with light petroleum (300 ml.) gave, from aqueous acetic acid–methanol, iso*euphadiene* (*ca.* 1 g.). Recrystallised from methylene dichloride–methanol this had m. p. 64—66°, $[\alpha]_D$ −30° (*c*, 1·70) (Found: C, 87·5; H, 12·4. $C_{30}H_{50}$ requires C, 87·75; H, 12·25%).

*iso*Euphadiene (3·0 g.) in methylene dichloride (50 ml.) was treated with ozone at −70° until the appearance of a faint blue colour. Glacial acetic acid (20 ml.) and zinc dust (3·0 g.) were added with stirring, and the stirring was continued for 3 hr. at 0—10°. The methylene dichloride was distilled over into 2 : 4-dinitrophenylhydrazine hydrochloride solution. The precipitate of acetone 2 : 4-dinitrophenylhydrazone (10%) was identified by m. p. and mixed m. p. (126°).

Dehydrogenation of iso*Euphadiene.*—*iso*Euphadiene (12 g.) and selenium powder (24 g.) were heated together at 350° for 48 hr The product was worked up as described above for the dehydrogenation of euphadiene. Chromatography over alumina and elution with light petroleum (250-ml. portions) gave: (i) an oil (1·5 g.), (ii) a solid (25 mg.), m. p. 82—92°, (iii) a solid (25 mg.), m. p. 100—106°, (iv) a trace of oil, and (v) a solid (25 mg.), m. p. 220—235°. Distillation of fraction (i) gave an oil, b. p. 100—120°/2 mm. Dissolution in ethanol and addition of picric acid gave 1 : 2 : 5-trimethylnaphthalene picrate, m. p. 133—135°. Recrystallisation from ethanol furnished pure material (140 mg.), m. p. and mixed m. p. 139—140° (Found: C, 57·0; H, 4·5; N, 11·4. Calc. for $C_{19}H_{17}O_7N_3$: C, 57·15; H, 4·5; N, 10·5%). The picrate was decomposed to give 1 : 2 : 5-trimethylnaphthalene, identified by m. p., mixed m. p., and absorption spectrum ($\lambda_{max.}$ 230, 278, 289, and 324 mμ, $\varepsilon_{max.}$ 115,000, 7500, 8600, and 1500). The authentic specimens of 1 : 2 : 5-trimethylnaphthalene and its picrate were kindly supplied by Professor Sir Ian Heilbron, D.S.O., F.R.S., to whom we express our best thanks. Examination of fractions (ii), (iii), and (v) gave no indication of 1 : 7 : 8-trimethylphenanthrene.

Bromination of the Diketone (XXIII; R = OAc, R′ = C_8H_{17}).—The bromination experiments were carried out as detailed by Barnes, Barton, Cole, Fawcett, and Thomas (*J.*, 1953, 571) except that the concentration of bromine was approx. 2 g. per 100 ml. of acetic acid. (The figure of 19 g. per 100 ml. of acetic acid given in that paper should read 1·9 g.) The product (100 mg.) from the bromination of the diketone in acetic acid (100 ml.) was refluxed with zinc dust (5 g.; added portionwise) for 2 hr. Crystallisation from methanol gave back the parent acetoxy-diketone (XXIII; R = OAc, R′ = C_8H_{17}) (m. p. and mixed m. p.).

Dehydrogenation of iso*Euphenyl Acetate with Selenium Dioxide.*—*iso*Euphenyl acetate (500 mg.) in acetic acid (45 ml.) was heated under reflux with selenium dioxide (250 mg.) in the minimum of water for 3 hr. Chromatography of the product over alumina and elution with 1 : 3 benzene–light petroleum gavė (from methanol) *iso*euphadienyl acetate, m. p. 92—94°, $[\alpha]_D$ +18° (*c*, 0·4), $\lambda_{max.}$ 246, 255, and 264 mμ (log ε 4·25, 4·35, and 4·15 respectively), undepressed in m. p. on admixture with an authentic specimen with the same constants prepared from *iso*euphenyl acetate oxide (Vilkas, *Bull. Soc. chim. France*, 1950, 582) (Found: C, 81·9; H, 11·4. Calc. for $C_{32}H_{50}O_2$: C, 82·0; H, 11·15%).

Hydrogenation of iso*Euphadienyl Acetate.*—*iso*Euphadienyl acetate, m. p. 90—92°, $[\alpha]_D$ +18° (*c*, 1·70) (200 mg.), in glacial acetic acid (20 ml.) was hydrogenated over platinum at 80° for 1 hr. Crystallisation of the product from absolute ethanol gave *iso*euphenyl acetate (140 mg.), m. p. 110—111°, $[\alpha]_D$ −9·0° (*c*, 2·3), undepressed in m. p. on admixture with an authentic specimen of m. p. 110—112°.

The hydrogenation product (120 mg.) was hydrolysed with lithium aluminium hydride (excess) in ether (40 ml.). Crystallisation of the product from nitromethane gave *iso*euphenol, m. p. and mixed m. p. 98—100°, $[\alpha]_D$ −17° (*c*, 2·55).

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