648. *Photochemical Transformations. Part XI.* The Photochemistry of Pentacyclic Triterpenoids with Diene Unsaturation in Ring* C.[1]

By R. L. Autrey, D. H. R. Barton, A. K. Ganguly, and W. H. Reusch.

Irradiation of methyl dehydroursolate acetate affords an isomeric triene, analogous to precalciferol, which isomerises thermally to a further triene comparable in its structure with calciferol itself. The generality of such cleavage is discussed in structural terms.

The photoisomerisation of steroidal 5,7-dienes (as I) is one of the most thoroughly studied of photochemical reactions.[2] It has been established that the initial photochemical act affords a triene (as II) [3] which subsequently isomerises purely thermally to the vitamin D type of triene (as III). These, and other aspects, of the photochemical behaviour of steroidal 5,7-dienes have been studied especially by Havinga and his colleagues.[4]

At the outset of the present investigations it seemed to us that the photochemical cleavage of a homoannular cyclohexadiene ring, such as that of (I) into (II), should be a general reaction, although according to Jeger, Redel, and Nowak [5] irradiation of dehydro-α-amyrin acetate (IV; R = Ac, R′ = Me) and of methyl dehydroursolate acetate (IV; R = Ac, R′ = CO_2Me) gave products that showed only terminal absorption at 220 mμ in the ultraviolet region and were therefore not the expected trienes (V; R = Ac, R′ = Me and CO_2Me, respectively). In fact, we quickly established that irradiation of methyl dehydroursolate acetate in boiling ether caused disappearance of the homoannular diene band near 280 mμ and appearance of a new band near 240 mμ which eventually reached an intensity of ε ~9000. Removal of the ether gave non-crystalline material with the same spectrum. Refluxing in ethanol solution without irradiation then led to the diminution and eventual disappearance of the 240 mμ band concomitant with the development of a new band at 261 mμ. Removal of the solvent at this stage then afforded a crystalline product shown in the sequel to have structure (VI: R = Ac, R′ = CO_2Me). For preparative purposes the process can be carried out in refluxing ethanol, irradiation being interrupted when the initial diene band has disappeared; the purely thermal isomerisation is subsequently allowed to proceed under reflux. Yields of approximately 75% can be attained.

The constitution of the triene (VI; R = Ac, R′ = CO_2Me) is based upon the following facts. The ultraviolet spectrum is consistent with a triene system,[6] and the infrared spectrum shows a band near 890 cm.$^{-1}$ assignable to ($>C=CH_2$). Ozonolysis of the triene gave formaldehyde, a crystalline dicarboxylic acid, and an oily keto-ester. The crystalline acid was shown to have structure (VIII; R = Ac, R′ = H) in the following way. Hydrolysis gave the hydroxy-dicarboxylic acid (VIII; R = R′ = H) which on methylation and benzoylation or 3,5-dinitrobenzoylation afforded the derivatives (VIII; R = acyl, R′ = Me). Authentic racemic benzoate dimethyl ester (VIII; R = Bz, R′ = Me) was readily prepared by oxidation of the synthetic keto-benzoate [7] (XI; R = Bz) with chromic acid to the acid (VIII; R = Bz, R′ = H), followed by methylation. Comparison of infrared spectra established identity. The neutral keto-ester, $[\alpha]_D$ −27°, was shown to have structure (IX; R = Me) by the following experiments. Vigorous alkaline hydrolysis

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* Part X, *J.*, 1961, 1215.

[1] Preliminary account: Autrey, Barton, and Reusch, *Proc. Chem. Soc.*, 1959, 55.

[2] Fieser and Fieser, " Steroids," Reinhold Publ. Corpn., New York, 1959, pp. 90 *et seq.*

[3] Velluz, Petit, Michel, and Rousseau, *Compt. rend.*, 1948, **226**, 1287; Velluz, Petit, and Amiard, *Bull. Soc. chim. France*, 1948, 1115; Velluz, Amiard, and Petit, *ibid.*, 1949, 501.

[4] Rappoldt and Havinga, *Rec. Trav. chim.*, 1960, 79, 369; and many earlier papers.

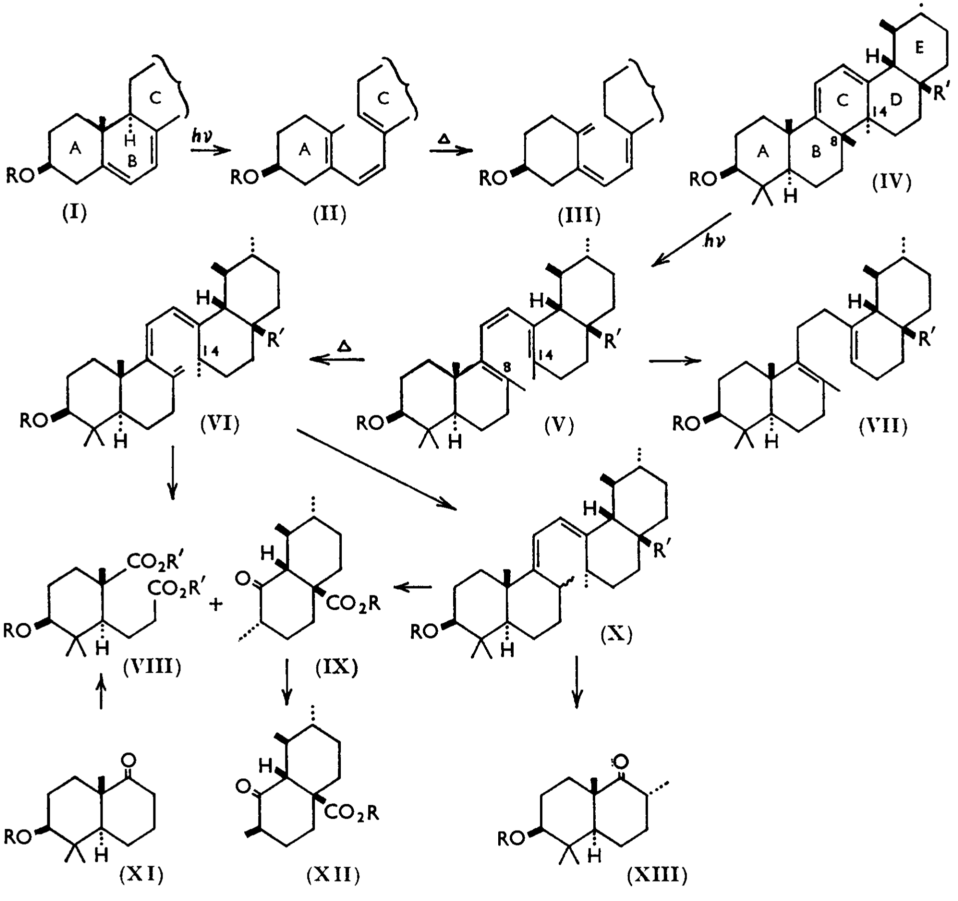
[5] Jeger, Redel, and Nowak, *Helv. Chim. Acta*, 1946, **29**, 1241.

[6] Fieser and Fieser, *op. cit.*, pp. 15 *et seq.*

[7] Sondheimer and Elad, *J. Amer. Chem. Soc.*, 1958, **80**, 1967; see also Gaspert, Halsall, and Willis, *J.*, 1958, 624; Kalvoda and Loeffel, *Helv. Chim. Acta*, 1957, **40**, 2340.

furnished a crystalline keto-acid which must be (XII; R = H) because of its constitution and of the way in which it is derived. Remethylation of the acid gave a different methyl ester which had $[\alpha]_D$ $-108°$. Since the keto-acid has certainly been equilibrated by the hydrolytic conditions we assign the more stable equatorial configuration to the α-methyl group as already indicated in the formula. The original keto-ester must therefore have the opposite (α-)configuration, as written in the formula (IX; R = Me). Isomerisation of the *cis*- to *trans*-decalone is, of course, excluded by the cogent arguments of Corey and Ursprung.[8]

Further proof of the constitution of the triene (VI; R = Ac, R′ = CO_2Me) was secured in the following way. Selective hydrogenation of the triene gave a dihydro-derivative (X; R = Ac, R′ = CO_2Me) which, although it could not be obtained crystalline, had the expected ultraviolet maximum at 250 mμ and no infrared band for a $>C{=}CH_2$ group. Ozonolysis gave the known [9] keto-acetate (XIII; R = Ac) as well as the same keto-ester (IX; R = Me) as was obtained in the earlier degradation.



We were especially interested in the nature of the photochemically produced intermediate with ultraviolet absorption near 240 mμ. Although this is an abnormally short wavelength for a triene,[10] nevertheless we suspected that the compound had structure

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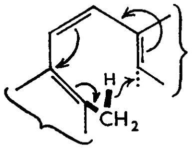
[8] Corey and Ursprung, *J. Amer. Chem. Soc.*, 1956, **78**, 183.

[9] Ruegg, Dreiding, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 889.

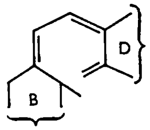
[10] Inhoffen, Brückner, Gründel, and Quinkert, *Chem. Ber.*, 1954, **87**, 1407; Inhoffen and Quinkert, *ibid.*, p. 1418; Verloop, Koevoet, and Havinga, *Rec. Trav. chim.*, 1957, **76**, 689; Harrison and Lythgoe, *J.*, 1958, 837.

(V; R = Ac, R′ = CO_2Me). In the ursolic series neither the 240 mμ material nor its derivatives could be crystallised. Indeed, the compound is too easily isomerised thermally to permit extensive manipulation. In the α-amyrin series, on the other hand, the diene (IV; R = Ac, R′ = Me) furnishes on irradiation a similar maximum near 240 mμ which is unaffected in refluxing ethanol. By conversion into the 3,5-dinitrobenzoate a crystalline compound (V; R = acyl, R′ = Me) was obtained. This showed a nuclear magnetic resonance spectrum indicative of allylic methyl (2) and vinyl hydrogen (2) as in the assigned formula. Hydrolysis gave a non-crystalline alcohol (V; R = H, R′ = Me) with $\lambda_{max.}$ 240 mμ (ε 9200) and no infrared band for a $>C=CH_2$ group. This was selectively hydrogenated to a dihydro-derivative (VII; R = H, R′ = Me) which had no selective ultraviolet absorption and afforded a crystalline 3,5-dinitrobenzoate. The latter showed allylic methyl, but no vinyl hydrogen, in its nuclear magnetic resonance spectrum. Per-acid titration of the 3,5-dinitrobenzoate confirmed that two ethylenic linkages were present and that cyclopropane formation was not involved in the photo-isomerisation.

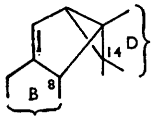
The photo-trienes (V; R = Ac, R′ = CO_2Me and Me) are assigned the expected *cis*-configuration, as already indicated, because irradiation with a tungsten lamp in the presence of iodine caused a shift of the maximum to longer wavelengths and greater intensities. This is a standard procedure for detecting a *cis*-isomer[11] and a suitable model experiment was run with calciferol to check our technique. The *cis*-configuration of the photo-trienes is so encumbered that the abnormal spectrum is readily understood. Indeed, the two methyl groups at positions 8 and 14 cannot be coplanar and it is possible that the 8-methyl group, which was originally β-oriented, retains its position above the 14-methyl group, which was originally α-oriented. This would explain the stereospecificity of the thermal rearrangement [see (XIV)] which would necessarily place hydrogen in the β-configuration at position 14 in the trienes, as in (VI). We cannot, however, explain why the other possible thermal isomerisation product (XV) is not formed in major amount, or why the photo-triene in the α-amyrin series (V; R = Ac, R′ = Me) is more stable than that in the ursolate series (V; R = Ac, R′ = CO_2Me).



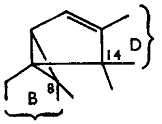
(XIV)



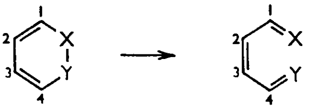
(XV)



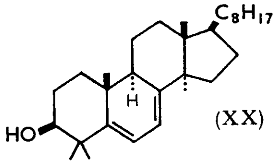
(XVI)



(XVII)



(XVIII) (XIX)



(XX)

In summary, it may be said that the photochemistry of the triterpenoid homoannular ring C dienes parallels that of the steroidal dienes.[12] The analogy may well extend to the products described by Jeger, Redel, and Nowak.[5] We were able to show that over-irradiation of the triene (V; R = Ac, R′ = CO_2Me) gave the photo-isomer previously described. This well-crystallised product was not formed on over-irradiation of the triene (VI; R = Ac, R′ = CO_2Me). The absorption spectra of the over-irradiation products are comparable with those of the suprasterols.[13] If structural analogy also pertains then

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[11] See, *inter al.*, Verloop, Koevoet, and Havinga, *Rec. Trav. chim.*, 1955, **74**, 1125; Inhoffen, Quinkert, Hess, and Erdmann, *Chem. Ber.*, 1956, **89**, 227; Verloop, Koevoet, van Moorselaar, and Havinga, *Rec. Trav. chim.*, 1959, **78**, 1004.

[12] See Havinga, de Koch, and Rappoldt, *Tetrahedron*, 1960, **11**, 276.

[13] Dauben, Bell, Hutton, Laws, Rheiner, and Urscheler, *J. Amer. Chem. Soc.*, 1958, **80**, 4116.

the compounds of Jeger, Redel, and Nowak[5] can be represented as in formula (XVI) or (XVII).

In our preliminary communication[1] we pointed out that the photochemical cleavage of steroidal ring B dienes, of triterpenoid ring C dienes, and of *ortho*-type cyclohexadienones[14] could all be fitted into a generalised scheme of the type (XVIII) ⟶ (XIX), a theme which we have developed further.[15] Obviously carbon atoms 1—4 can bear a wide variety of substituents and can themselves be replaced by other hetero-atoms. Also, there is considerable scope for variation in X and Y. Recently, it has been reported[16] that α-pyrones fall into this category, as does one example of a conjugated pyran.[17] So far as homoannular cyclohexadienes are concerned cyclohexa-1,3-diene behaves as expected,[18] as does α-phellandrene.[18] It will be of interest to see how far this simple structural theme can be developed.

The calciferol analogue (VI; R = H, R′ = CO_2Me) obtained by mild alkaline hydrolysis of the corresponding acetate had no significant biological activity (<1/10,000 that of calciferol). We report also that irradiation of 7-dehydro-4,4,14-trimethylcholesterol[19] (XX) gave a product with a similar lack of activity. We thank Messrs. Glaxo Laboratories Ltd. for these tests.

EXPERIMENTAL

M. p.s were taken on the Kofler block. Unless specified to the contrary, $[\alpha]_D$ refer to $CHCl_3$ and ultraviolet absorption spectra to EtOH solutions, and infrared absorption spectra to Nujol mulls. Microanalyses were carried out by Miss J. Cuckney and her colleagues. Light petroleum refers to the fraction of b. p. 40—60°. Nuclear magnetic resonance spectra were kindly determined and interpreted by Dr. J. W. Lown.

Irradiation of Methyl Dehydroursolate Acetate (IV; R = Ac, R = CO_2Me).—Methyl dehydroursolate acetate[20] (1·0 g.) in ethanol (400 ml.) was irradiated in a Pyrex-glass flask with a bare mercury-arc lamp (125 w). The flask was placed over the lamp so that the solvent refluxed gently. All irradiations were conducted under oxygen-free nitrogen. The course of the irradiation was determined by ultraviolet spectroscopy. The band at 283 mμ of the starting material declined and new bands appeared at ~240 and ~260 mμ. Irradiation was interrupted when the band at 260 mμ had ε ~10,000 and that at 240 mμ had ε ~8000. The 283 mμ band had by then essentially disappeared. The mixture was then refluxed under nitrogen for 2 hr., the 240 mμ band disappearing and the 260 mμ band attaining ε ~15,000. The combined ethanolic solutions from two such irradiations were concentrated *in vacuo* to about 25 ml. and left at room temperature for 12 hr. Starting material (about 250 mg.) crystallised and was removed. The filtrate, left at 0° overnight, gave prisms, m. p. 144—147°, $\lambda_{max.}$ 261 mμ (ε 18,000). Filtration and removal of the residual solvent *in vacuo* afforded a yellow gum which was chromatographed in light petroleum over acid-washed alumina (Grade II; 60 g.). Elution with 9 : 1 and 4 : 1 light petroleum–benzene gave oils with $\lambda_{max.}$ 240 mμ (ε 8200 and 7700 respectively) which were not examined further. Elution with 1 : 1 light petroleum–benzene gave further material, with $\lambda_{max.}$ at 261 mμ. This was combined with the product obtained by direct crystallisation (see above) (1·53 g.). Recrystallisation from ether–methanol gave *methyl pyrophotodehydroursolate acetate* (VI; R = Ac, R′ = CO_2Me) (57%), m. p. 152—153°, $[\alpha]_D$ −85° (*c* 0·87 in CCl_4), $\lambda_{max.}$ 215 and 261 mμ (ε 16,000 and 19,700 respectively), $\lambda_{min.}$ 230 mμ (ε 9400), $\nu_{max.}$ (in CCl_4) 1727, 1628, 1239, and 895 $cm.^{-1}$ (Found: C, 77·7; H, 9·85. $C_{33}H_{50}O_4$ requires C, 77·6; H, 9·85%).

Ozonolysis of Methyl Pyrophotodehydroursolate Acetate (VI; R = Ac, R′ = CO_2Me).—(a) *Characterisation of formaldehyde.* The triene (53 mg.) in purified methylene dichloride (10 ml.

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[14] Barton and Quinkert, *Proc. Chem. Soc.*, 1958, 197; *J.*, 1960, 1.

[15] Barton, *Helv. Chim. Acta*, 1959, **42**, 2604.

[16] de Mayo, in " Advances in Organic Chemistry," ed. Raphael, Taylor, and Wynberg, Interscience Publ. Inc., New York, 1960, Vol. II, p. 394.

[17] Büchi and Yang, *Helv. Chim. Acta*, 1955, **38**, 1338; *J. Amer. Chem. Soc.*, 1957, **79**, 2318.

[18] de Koch, Minnaard, and Havinga, *Rec. Trav. chim.*, 1960, **79**, 922; see also Barton, ref. 15, and compare Srinivasan, *J. Amer. Chem. Soc.*, 1960, **82**, 5063.

[19] Barton and Thomas, *J.*, 1953, 1842.

[20] Ruzicka, Jeger, and Redel, *Helv. Chim. Acta*, 1943, **26**, 1235.

was ozonised at −60° for 30 min. Zinc dust (1·0 g.) was added with stirring and the mixture allowed to attain room temperature. After filtration into distilled water the product was steam-distilled into aqueous dimedone, and the methylene dichloride boiled off. This afforded the dimedone–formaldehyde derivative (6 mg.), identified by m. p., mixed m. p., and crystal form. A control experiment gave no formaldehyde.

(b) *Isolation of major fragments.* The triene (365 mg.) in dry ethyl acetate (70 ml.) was ozonised at −5° until all triene absorption had disappeared (2 hr.). Water (5 ml.) was added and the ethyl acetate boiled off. The aqueous solution was made alkaline with sodium carbonate and treated with 10% hydrogen peroxide (3 ml.) on the steam-bath for 10 min. Extraction with ether gave a neutral fraction (see below). Acidification and further extraction with ether gave an acidic fraction which crystallised from ethyl acetate–cyclohexane as prisms, m. p. 163—178° (68 mg.). Sublimation at 10^{-6} mm. and recrystallisation from ether–light petroleum afforded the *acetoxy-dicarboxylic acid* (VIII; R = Ac, R′ = H), m. p. 180—185°, $[\alpha]_D$ ±0° (*c* 1·07) (Found: C, 59·9; H, 8·15. $C_{15}H_{24}O_6$ requires C, 60·0; H, 8·05%). Saponification with 5% ethanolic potassium hydroxide under reflux gave the corresponding *hydroxy-dicarboxylic acid* (VIII; R = R′ = H), m. p. (rhombic prisms from ethyl acetate–chloroform) 214—217° decomp., $[\alpha]_D$ −9° (*c* 0·62 in dioxan) (Found: C, 60·45; H, 8·75. $C_{13}H_{22}O_5$ requires C, 60·45; H, 8·6%). Treatment with ethereal diazomethane and then with benzoyl chloride–pyridine afforded the corresponding *benzoate dimethyl ester* (VIII; R = Bz, R′ = Me). Recrystallised from methylene dichloride–light petroleum this formed needles, m. p. 100—101·5°, $[\alpha]_D$ +14° (*c* 2·40 in CCl_4), $\lambda_{max.}$ 230, 274, and 282 mμ (ε 12,700, 890, and 710 respectively) (Found: C, 67·85; H, 7·85. $C_{22}H_{30}O_6$ requires C, 67·65; H, 7·75%). Similarly methylation with ethereal diazomethane followed by 3,5-dinitrobenzoylation [21] gave the *dimethyl ester* 3,5-*dinitrobenzoate.* This crystallised from ether–light petroleum as needles, m. p. 100—102° (Found: C, 54·6; H, 5·6. $C_{22}H_{28}N_2O_{10}$ requires C, 55·0; H, 5·85%).

The neutral fraction from the ozonolysis (see above) was combined with that from a further ozonolysis of 242 mg. of triene to give a viscous, pale yellow oil (289 mg.). Distillation at 120°/4 × 10^{-5} mm. furnished the keto-ester (IX; R = Me) (125 mg.) as a colourless, viscous oil, $[\alpha]_D$ −27° (*c* 2·14), $\nu_{max.}$ (in CS_2) 1733 and 1710 cm.$^{-1}$. Saponification with an aqueous-ethanol (6 ml.; 80%) solution of potassium hydroxide (90 mg.) under reflux (oxygen-free nitrogen) for 3 hr. and separation into acidic and neutral fractions afforded, in the acidic portion, crystalline 1β,2α,7β-*trimethyl*-8-*oxo*-cis-*decalin*-4αβ-*carboxylic acid* (XII; R = H) (173 mg.). After sublimation at 120°/4 × 10^{-5} mm. and crystallisation from ether–light petroleum this formed irregular crystals which melted partially at 143° and then resolidified as plates, m. p. 160—163°, $[\alpha]_D$ −97° (*c* 2·24), $\nu_{max.}$ 1718 and 1681 cm.$^{-1}$ (Found: C, 70·75; H, 9·45. $C_{14}H_{22}O_3$ requires C, 70·55; H, 9·3%). Treatment with ethereal diazomethane gave the oily keto-ester (XII; R = Me), b. p. 118°/2 × 10^{-5} mm., $[\alpha]_D$ −108° (*c* 1·19).

Synthesis of Racemic Methyl β-(3β-*Benzoyloxy*-6α-*methoxycarbonyl*-2,4,6-*trimethyl*-β-*cyclohexyl*)*propionate* (VIII; R = Bz, R′ = Me).—The racemic ketone-benzoate [7] (XI; R = Bz) (21 mg.) was taken up in 0·0784N-chromium trioxide in acetic acid (8·4 ml.) and warmed on the steam-bath until an aliquot part showed that the theoretical amount of oxidant had been consumed. The excess of chromium trioxide was destroyed by sulphur dioxide, and the solvent removed *in vacuo.* Addition of water (1·0 ml.) and extraction into ether gave the dicarboxylic acid benzoate (VIII; R = Bz, R′ = H). Sublimation and crystallisation from ethyl acetate–cyclohexane furnished a specimen (44%), m. p. 198—200°, which with an excess of diazomethane gave the racemic *benzoate dimethyl ester* (VIII; R = Bz, R′ = Me). This formed needles (from methylene dichloride–light petroleum), m. p. 101—103°, mixed m. p. 95—103° with optically active material (Found: C, 67·7; H, 7·85. $C_{22}H_{30}O_6$ requires C, 67·65; H, 7·75%). The infrared spectra of the racemic and the optically active material were identical (CCl_4; 22 bands).

Methyl Dihydropyrophotodehydroursolate Acetate (X; R = Ac, R′ = CO_2Me).—Methyl pyrophotodehydroursolate acetate (VI; R = Ac, R′ = CO_2Me) (100 mg.) in ethanol (5 ml.) was hydrogenated over 10% palladised strontium carbonate (Johnson Matthey) until 1 mol. of hydrogen had been consumed. The product was chromatographed over alumina (Grade III; 5 g.). Elution with 1 : 10 ether–light petroleum and sublimation at 140°/2 × 10^{-5} mm. gave the required dihydro-compound (X; R = Ac, R′ = CO_2Me) as a colourless gum, $\lambda_{max.}$ 250 mμ (ε 12,800), $[\alpha]_D$ +82° (*c* 0·53), $\nu_{max.}$ 1724 and 1235 cm.$^{-1}$, no absorption at 893 cm.$^{-1}$.

This dihydro-compound (400 mg.) in methylene dichloride (25 ml.) was ozonised at −5°

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[21] Brewster and Ciotti, *J. Amer. Chem. Soc.*, 1955, **77**, 6214.

until the ultraviolet absorption band at 250 mμ had disappeared. Water (3 ml.) was added and the methylene dichloride removed *in vacuo*. The product was saponified with 1 : 5 aqueous-ethanolic potassium hydroxide (400 mg. in 24 ml.) under reflux (oxygen-free nitrogen) for 4 hr. and separated into acidic (160 mg.) and neutral (160 mg.) fractions. The acidic fraction, on sublimation and crystallisation from ether–light petroleum, gave the keto-acid (XII; R = H), identified by m. p., mixed m. p., crystal form, and infrared spectrum. The neutral fraction was acetylated with pyridine–acetic anhydride and then sublimed at 10^{-6} mm. to give crystalline acetoxy-ketone (XIII; R = Ac). Recrystallised from ether–light petroleum this formed needles, m. p. 128—129°, $[\alpha]_D$ −10° (*c* 0·70), $\nu_{max.}$ 1724 and 1703 cm.$^{-1}$ (Found: C, 72·45; H, 9·7. Calc. for $C_{16}H_{26}O_3$: C, 72·15; H, 9·85%). The constants given in the literature [9] are m. p. 128—129°, $[\alpha]_D$ −12° (*c* 0·76).

Photodehydro-α-amyrin 3,5-*Dinitrobenzoate* (V; R = 3,5-Dinitrobenzoyl, R′ = Me).—Dehydro-α-amyrin [20] (IV; R = H, R′ = Me) (500 mg.) was irradiated in anhydrous ether (400 ml.) as outlined above. The band at 281 mμ of the starting material declined and a new band appeared at 240 mμ reaching a maximum intensity of ε 8000—9000. Removal of solvent *in vacuo* gave a foam showing $\lambda_{max.}$ 240 mμ (ε 8200) with no infrared band near 890 cm.$^{-1}$. This material, which did not crystallise, was converted into its 3,5-dinitrobenzoate by Brewster and Ciotti's method.[21] Chromatography over alumina (Grade IV), elution with 1 : 1 light petroleum–benzene and crystallisation from methanol–acetone and then from acetone afforded *photodehydro-α-amyrin* 3,5-*dinitrobenzoate* (V; R = 3,5-dinitrobenzoyl, R′ = Me) as needles, m. p. 116—121°, $[\alpha]_D$ +335° (*c* 0·77 in CCl_4), $\lambda_{max.}$ 213 mμ (ε 51,200), shoulder at 220 mμ (ε 47,400), no infrared absorption at 890 cm.$^{-1}$ (Found: C, 71·7; H, 8·3. $C_{37}H_{50}N_2O_6$ requires C, 71·8; H, 8·15%).

Dihydrophotodehydro-α-amyrin 3,5-*Dinitrobenzoate* (VII; R = 3,5-Dinitrobenzoyl, R′ = Me).—Photodehydro-α-amyrin 3,5-dinitrobenzoate (see above) (72 mg.) was refluxed for 45 min. with aqueous-ethanolic 1% potassium hydroxide (5 ml.). The neutral product, photodehydro-α-amyrin, had $\lambda_{max.}$ 240 mμ (ε 9200) and no infrared band near 890 cm.$^{-1}$ but it did not crystallise. This product (98 mg.) in ethanol (5 ml.) was hydrogenated over 10% palladised charcoal (Baker) until 1·2 mol. had been taken up (good selectivity). The product, which had only end-absorption at 203 mμ (ε 10,000), was 3,5-dinitrobenzoylated as above. The product, chromatographed over alumina (Grade III) with elution by 1 : 1 light petroleum–benzene, crystallised from acetone–methanol, to give *dihydrophotodehydro-α-amyrin* 3,5-*dinitrobenzoate* (VII; R = 3,5-dinitrobenzoyl, R′ = Me) as needles, m. p. 163—164°, $\lambda_{max.}$ (in cyclohexane) 211 mμ (ε 33,580), shoulder 227 (ε 26,550) (Found: C, 71·4; H, 8·1; N, 4·3. $C_{37}H_{52}O_6N_2$ requires C, 71·6; H, 8·45; N, 4·5%). Titration with perphthalic acid showed the presence of two ethylenic linkages.

Iodine-catalysed Isomerisation of Photodehydro-α-amyrin.—Photodehydro-α-amyrin (V; R = H, R′ = Me) (4·8 mg.) in anhydrous ether (500 ml.) containing a trace of pyridine and iodine (0·01 mg.) was irradiated [11] with a tungsten lamp until maximum absorption was reached (45 min.). The irradiated solution, freed from iodine and pyridine, was evaporated to dryness *in vacuo* to an oil showing $\lambda_{max.}$ 253 mμ (ε 13,000).

In a parallel model experiment calciferol, $\lambda_{max.}$ 265 mμ (ε 18,000), was irradiated [11] as above. The product showed $\lambda_{max.}$ 272 mμ (ε 23,200).

Over-irradiation of Methyl Pyrophotodehydroursolate Acetate (VI; R = Ac, R′ = CO_2Me).—(*a*) Methyl dehydroursolate acetate (IV; R = Ac, R′ = Me) (244 mg.) in anhydrous ether (300 ml.) was irradiated in a Pyrex flask (500 ml.) cooled under running water so that the temperature of the solution did not exceed 10°. During the irradiation the ultraviolet absorption maximum changed from 282 mμ to that expected of methyl photodehydroursolate acetate (V; R = Ac, R′ = Me) [$\lambda_{max.}$ 240 mμ (ε 10,000), $\lambda_{min.}$ 230 mμ (ε 9900) end-absorption] and then, on continued irradiation, the absorption at 240 mμ declined and the spectrum changed to that of methyl lumidehydroursolate acetate (see below). The ether was removed *in vacuo* and the product crystallised from acetone–methanol, to furnish methyl lumidehydroursolate acetate (52 mg.), m. p. 163—164°, end absorption with ε 9300 at 220 mμ and 1100 at 250 mμ. In a second experiment in which the ether was allowed to reflux during the irradiation methyl dehydroursolate acetate (102 mg.) gave the same methyl lumidehydroursolate acetate (44 mg.) (Found: C, 77·85; H, 9·4. Calc. for $C_{33}H_{50}O_4$: C, 77·6; H, 9·85%). Jeger, Redel, and Nowak [5] record m. p. 162—163° for the latter compound.

(*b*) Methyl pyrophotodehydroursolate acetate (VI; R = Ac, R′ = Me) (244 mg.) was irradiated <10° as described above. The absorption of the triene changed smoothly to a broad curve showing end-absorption only, with ε 8600 at 220 mμ. Removal of the solvent *in vacuo* gave an oil which did not crystallise even after chromatography. The various fractions showed infrared spectra lacking several bands characteristic of methyl lumidehydroursolate acetate.

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