609. *The Chemistry of the Triterpenes and Related Compounds. Part XXIX.* The Chemistry of Butyrospermol.*

By M. C. Dawson, T. G. Halsall, E. R. H. Jones, G. D. Meakins, and P. C. Phillips.

Butyrospermol has been shown to be 9ξ(H)-eupha-7 : 24-dien-3β-ol (XII). The configuration at $C_{(9)}$ is discussed.

Butyrospermol was first characterised as such by Heilbron, Jones, and Robins [1] who isolated it from shea-nut fat, although it is now certain that basseol, which was earlier isolated from the same source by Heilbron, Moffet, and Spring [2] is identical with it.[3-5] It is a tetracyclic diethenoid secondary alcohol with an easily hydrogenable double bond present in an *iso*propylidene group.[1] The other double bond could not be hydrogenated but it reacted with perbenzoic acid. Seitz and Jeger [6] confirmed these results and prepared the hydrocarbon butyrospermene corresponding to dihydrobutyrospermol. They concluded from the infrared spectrum of the hydrocarbon that the less reactive double bond was fully substituted.

Dawson, Halsall, Jones, and Robins [3] found that the less reactive double bond was isomerised under mild acidic conditions (treatment with chloroformic hydrogen chloride for two hours), the dihydro-acetate giving dihydro*iso*butyrospermyl acetate. The double bond in the isomer was reported as being unreactive towards perbenzoic acid although it is now clear that this observation was erroneous. The evidence described above together with the similar light absorption intensities in the ultraviolet region of dihydrobutyrospermol and its isomer led to the suggestion that the isomerisation was analogous to that of lanostenyl acetate to *iso*lanostenyl acetate with the double bond moving from a tetra- to a tri-substituted position.[3]

Careful examination of the infrared spectra of a number of derivatives of dihydrobutyrospermol and dihydro*iso*butyrospermol showed that in the former group there were always bands at *ca.* 830 cm.$^{-1}$ characteristic of a *tri*substituted bond,[7] but that in the case of the latter bands did not appear at this frequency, indicating that the double bond was now tetrasubstituted (cf. Table). The ultraviolet absorption data referred to earlier are equally consistent with this new conclusion provided that the trisubstituted double bond is *exo*cyclic and the tetrasubstituted double bond is *endo*cyclic.

* Part XXVIII, *J.*, 1956, 2904.

[1] Heilbron, Jones, and Robins, *J.*, 1949, 444.
[2] Heilbron, Moffet, and Spring, *J.*, 1934, 1583.
[3] Dawson, Halsall, Jones, and Robins, *J.*, 1953, 586.
[4] Dawson, Halsall, Jones, Meakins, and Phillips, *Chem. and Ind.*, 1955, 918.
[5] Irvine, Lawrie, McNab, and Spring, *J.*, 1956, 202ϑ.
[6] Seitz and Jeger, *Helv. Chim. Acta*, 1949, **32**, 1626.
[7] Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954, p. 44.

Infrared absorption frequencies (in cm.$^{-1}$) of bands between 800 and 850 cm.$^{-1}$ (in carbon disulphide).

Dihydrobutyrospermone	818*w*, 827*m*, 835*s*	Dihydrobutyrospermyl acetate ...	826*m*, 840*vw*
Dihydrobutyrospermol ...	827*m*, 840*w* (in Nujol)	Dihydro*iso*butyrospermyl acetate (IX)	no band
Dihydro*iso*butyrospermol	no band		807*w*, 830*s*

When dihydrobutyrospermyl acetate was treated with an excess of perbenzoic acid in chloroform the main product was an αβ-unsaturated ketone which was, rather surprisingly, 7-oxoeuph-8-enyl acetate (I). This result, together with the infrared spectral data, is consistent only with dihydrobutyrospermol's being either (II; R = H) or (III; R = H), *i.e.*, having a euphane-type structure. The unsaturated ketone (I) is probably formed *via* the diene acetate (IV), produced from the initial epoxide by traces of hydrogen chloride present in the chloroform used as solvent. The diene then forms a 7 : 8-epoxide which rearranges to (I). With only one mol. of perbenzoic acid the dihydro-acetate (II or III) was converted into the diene acetate (IV). With this knowledge the identification of dihydro*iso*butyrospermyl acetate [3] as euph-8-enyl acetate (V) [8-11] quickly followed. In addition dihydrobutyrospermyl acetate was isomerised by platinum in acetic acid in hydrogen to euph-8-enyl acetate (V).

[This observation explains why " dihydrobasseol acetate " (bassenyl acetate) [12] and dihydrobutyrospermyl acetate are not identical. The latter was formed by hydrogenation of butyrospermyl acetate in a neutral solvent (ethyl acetate) when only the *iso*propylidene grouping is affected. The former was prepared by hydrogenation of basseol (butyrospermyl) acetate in acetic acid. Under these conditions isomerisation of the nuclear double bond should occur and euph-8-enyl acetate should be formed. " Dihydrobasseol acetate " has in fact been shown to be euph-8-enyl acetate.[13]]

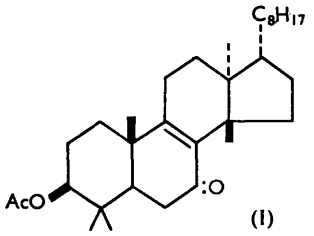
At first sight the formation of euph-8-enyl acetate from dihydrobutyrospermyl acetate by acidic isomerisation is surprising since it is well known that euph-8-enyl acetate is converted by acids into *iso*euphenyl acetate.[14] However, the experimental conditions in the two cases are quite different, euph-8-enyl acetate being formed from dihydrobutyrospermyl acetate by treatment with chloroformic hydrogen chloride for two hours, whereas the conversion into *iso*euphenyl acetate requires several days. Use was made of these differences to prove that *iso*butyrospermyl acetate [3] is eupha-8 : 25-dienyl acetate (VI). Euphyl acetate (VII) was treated with chloroform–hydrogen chloride for two hours. Under these conditions only addition of hydrogen chloride to the *iso*propylidene group should occur. The resulting product was dehydrochlorinated with boiling dimethylaniline, conditions which are known to lead to the formation of the *iso*propenyl group,[3] and eupha-8 : 25-dienyl acetate (VI) was obtained. It was identical with *iso*butyrospermyl acetate.

At this stage in our work Professor F. S. Spring kindly informed us that he and his colleagues had also concluded that dihydro*iso*butyrospermyl acetate was euph-8-enyl acetate and that they considered dihydrobutyrospermol to be (II), (III), or (VIII).[15] The last structure can, however, be excluded. Treatment of dihydrobutyrospermol with phosphorus pentachloride brings about the typical retropinacolinic dehydration to give the hydrocarbon (IX) which gives acetone on ozonolysis. The ultraviolet absorption spectrum of (IX) shows the absence of the diene chromophore which would be expected if (VIII) were correct.

The position of the nuclear double bond in butyrospermol was next shown to be as in (II). Dihydrobutyrospermyl acetate was isomerised in alcohol-free chloroform with deuterium chloride to give a deuterated euph-8-enyl acetate which has to be either (X) or (XI) depending on whether butyrospermol is (II; R = H) or (III; R = H). The presence of deuterium in the isomerisation product was indicated by the band at 2143

[8] Barton, McGhie, Pradhan, and Knight, *Chem. and Ind.*, 1954, 1325; *J.*, 1955, 876.
[9] Arigoni, Viterbo, Dünnenberger, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1954, **37**, 2306.
[10] Ménard, Wyler, Hiestand, Arigoni, Jeger, and Ruzicka, *ibid.*, 1955, **38**, 1517.
[11] Warren and Watling, *Chem. and Ind.*, 1956, 24.
[12] Beynon, Heilbron, and Spring, *J.*, 1937, 989.
[13] Dupont, Dulou, and Vilkas, *Bull. Soc. chim. France*, 1949, **16**, 809.
[14] Vilkas, Dupont, and Dulou, *ibid.*, p. 813.
[15] Irvine, Lawrie, McNab, and Spring, *Chem. and Ind.*, 1955, 626.

cm.$^{-1}$ in its absorption spectrum determined in carbon tetrachloride. Oxidation of this deuteroeuphenyl acetate with chromic acid (2 atoms of oxygen per molecule of euphenyl acetate) in acetic acid gave 7-oxoeuph-8-enyl acetate (I). The infrared spectrum of this ketone, determined under precisely the same conditions as were used for the determination



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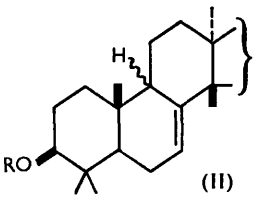

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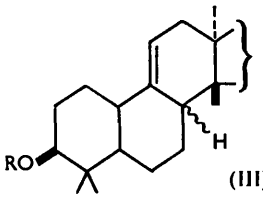

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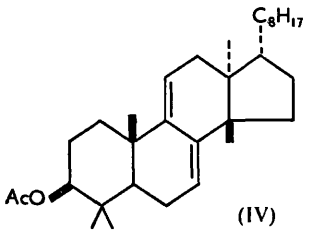

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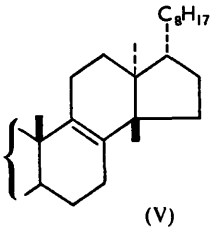

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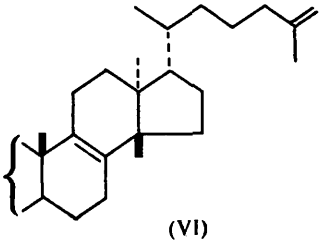
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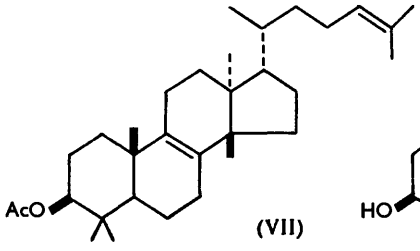

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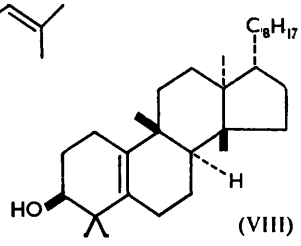

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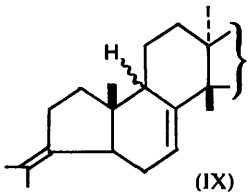


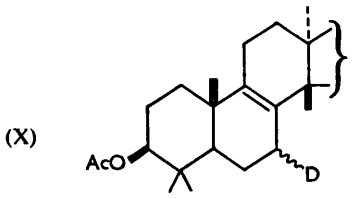
(IX)

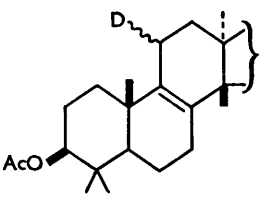
of the spectrum of the starting material, revealed that it contained no deuterium. The conclusion to be drawn is that the deuteroeuphenyl acetate is (X), the deuterium at $C_{(7)}$ being lost on oxidation to the 7-oxo-derivative, and hence that dihydrobutyrospermyl acetate is (II; R = Ac) and butyrospermol (XII).

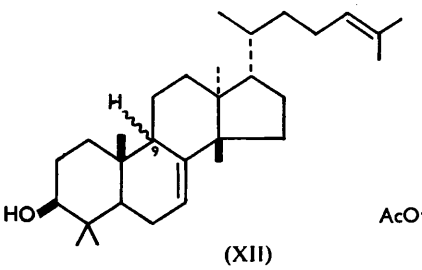
This conclusion can be criticised on the following grounds. If the conversion of euph-8-enyl acetate into the 7-oxo-derivative involves the formation of the intermediate eupha-7 : 9(11)-dienyl acetate then the deuteroeuphenyl acetate might be (XI) which it must be assumed loses deuterium stereospecifically during the formation of the diene. The final product would then be void of deuterium. However, this critism is not valid as it has been shown that the main path followed by the oxidation reaction does not involve the diene.

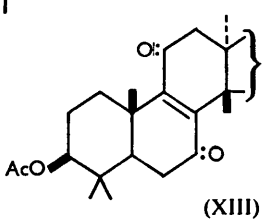
Euph-8-enyl acetate (V) was oxidised with chromic acid (just over 2 atoms of oxygen per molecule of euphenyl acetate) in acetic acid. The composition of the mixture of oxidation products, estimated on the basis of their different ultra-violet absorption maxima, was diene acetate (IV) (3%), αβ-unsaturated keto-acetate (I) (36%), diketo-acetate (XIII) (30%), together with some starting material, the last being isolated chromatographically. When eupha-7 : 9(11)-dienyl acetate was oxidised under similar conditions, only 1 oxygen atom per molecule of diene being used to allow for its higher oxidation state, a product was obtained which contained 7 : 11-dioxoeuph-8-enyl acetate (25%), starting material (diene, 45%), and only a trace of 7-oxoeuph-8-enyl acetate. These compounds account for only about 75% of the chromic acid used. It is likely that other products,

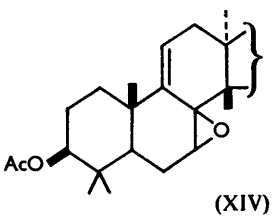
e.g., epoxides such as (XIV), which do not absorb ultraviolet light above 2200 Å were present. Evidence for this suggestion was obtained by treating the oxidation product with boron trifluoride in ether; the amount of 7 : 11-dioxoeuph-8-enyl acetate was then raised to *ca.* 30% and that of 7-oxoeuph-8-enyl acetate to 6%. It is possible that some



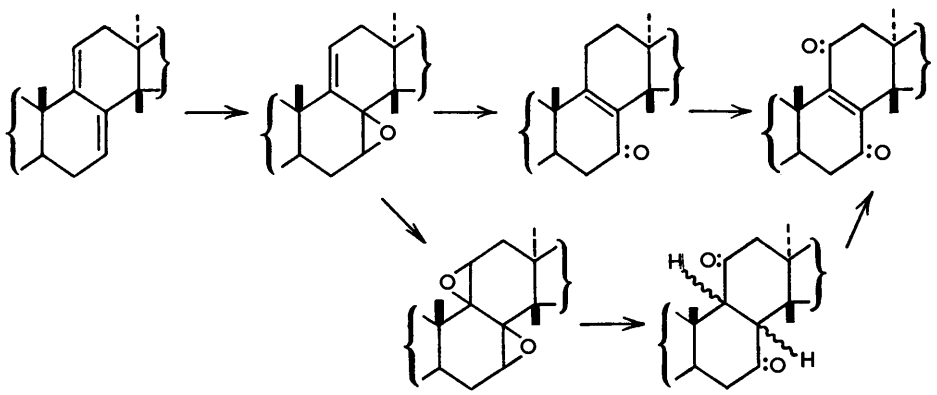








7 : 11-dioxoeuphanyl acetate was also present if it is assumed that the oxidation proceeds in the manner shown.

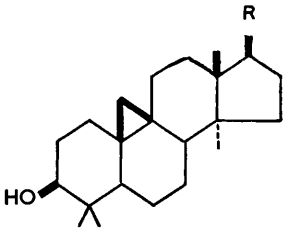


From these results it is clear that if chromic acid oxidation of euph-8-enyl acetate proceeds predominantly to the diene acetate which is subsequently oxidised, the ratio of 7 : 11-diketone to 7-ketone in the final product should be at least 5 : 1. In fact, the amount of the 7-oxo-derivative exceeds that of the 7 : 11-dioxo-derivative, while only a small amount of eupha-7 : 9(11)-dienyl acetate is formed. It is clear that the oxidation of euph-8-enyl acetate can proceed to only a small extent through the 7 : 9(11)-diene.

With the structure of butyrospermol now restricted to the two $C_{(9)}$ epimers of (XII) there remains the problem of the configuration at $C_{(9)}$. Barton, McGhie, Pradhan, and Knight [8] have shown that Wolff–Kishner reduction of 7-oxoeuph-8-enyl acetate followed by reacetylation gives a Δ^7-euphenyl acetate. This is not identical with dihydrobutyrospermyl acetate, and hence derivatives of both the $C_{(9)}$ epimers are known.

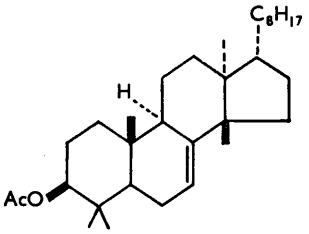
One striking feature of the chemistry of butyrospermol is that on oxidation of the hydroxyl to a keto-group there is an unusual negative shift in rotation ($\Delta M_D \approx -120°$),

similar to those found with *cyclo*artenol (XV) [16,17] and *cyclo*laudenol (XVI).[18] Barton [19] has suggested that this correlation may be significant. Another similarity between *cyclo*artenol and butyrospermol is that the corresponding ketones give only a very slight colour when subjected to the Zimmermann test (cf. Barton and Seoane [20]). One unique feature of *cyclo*artenol and *cyclo*laudenol as compared with other tetracyclic triterpenes is a 9β-substituent and in a preliminary communication [4] we tentatively suggested that the 9β-epimer of (XII) was to be preferred for butyrospermol. Evidence may, however, be



(XV); R = C_8H_{15}

(XVI); R = C_9H_{17}



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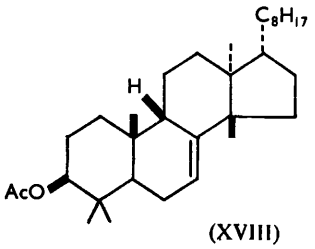

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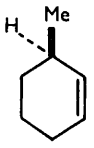

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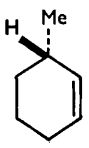

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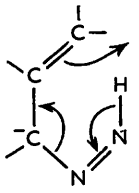

(XXI)

deduced from other molecular-rotation data which points to the 9α-configuration. If 9α(H)-euph-7-enyl and 9β(H)-euph-7-enyl acetates (XVII) and (XVIII) are regarded as a pair of substituted 3-alkyl*cyclo*hexenes (cf. XIX and XX) then the one with the more negative rotation should be the 9β-isomer (XVIII) corresponding to (XX) (cf. Mills [21]). The molecular rotations of dihydrobutyrospermyl acetate and of the Δ^7-euphenyl acetate obtained by Wolff–Kishner reduction are +62° and −202°, and on this basis butyrospermol would be given the 9α-configuration. Inspection of models indicates that only the 9β-epimer (XVIII) can exist in an all-chair type conformation and should be the more stable. Unfortunately, it is not known whether the Wolff–Kishner product is the more stable epimer because the mechanism of the reduction probably involves a cyclic transition state (cf. XXI) and such reactions do not always lead to the more stable isomer. At present therefore more evidence is required before a final decision on the configuration at $C_{(9)}$ can be made.

Experimental

Rotations were determined in chloroform at room temperature. M. p.s were determined on a Kofler block. The alumina used for chromatography had an activity I—II unless otherwise stated. Light petroleum refers to the fraction with b. p. 60—80°.

[16] Barton, Page, and Warnhoff, *J.*, 1954, 2715.
[17] Irvine, Henry, and Spring, *J.*, 1955, 1316.
[18] Henry, Irvine, and Spring, *ibid.*, p. 1607.
[19] Barton, *J.*, 1951, 1444.
[20] Barton and Seoane, *J.*, in the press.
[21] Mills, *J.*, 1952, 4976.

Butyrospermol was isolated from shea-nut fat by the method of Heilbron *et al.*[1] Dihydrobutyrospermyl acetate was more readily prepared by taking the second crop of crystals obtained from the acetylation of the non-saponifiable matter from shea-nut fat (cf. ref. 1) and hydrogenating it in ethyl acetate, using a platinum catalyst. The resulting mixture of unchanged β-amyrin acetate and dihydrobutyrospermyl acetate was then easily separated, the latter being more easily eluted.

Reduction of Dihydrobutyrospermone with Sodium Borohydride.—Sodium borohydride (40 mg.) in a little water was added to dihydrobutyrospermone (156 mg.) in dioxan (40 c.c.), and the mixture was kept at 20° for 1·5 hr. After dilution with water, extraction with ether yielded a product (136 mg.) which was adsorbed from benzene on alumina (15 g.). Elution with benzene–ether (1 : 1; 200 c.c.) gave dihydrobutyrospermol which after crystallisation from nitromethane had m. p. 113·5—115°, undepressed on admixture with an authentic sample (m. p. 114·5—116°), $[\alpha]_D$ −14° (*c*, 1·05).

Action of Phosphorus Pentachloride on Dihydrobutyrospermol.—Phosphorus pentachloride (600 mg.) was added to dihydrobutyrospermol (856 mg.) in dry light petroleum (80 c.c.). After evolution of hydrogen chloride had ceased (5 min.) water was added. The light petroleum phase was washed several times with water, dried (Na_2SO_4), and run on to alumina (40 g.). Elution with light petroleum (200 c.c.) gave a fraction (814 mg.) which was crystallised from ethyl acetate–methanol, giving *γ-butyrospermadiene* (IX), m. p. 79—81·5°, $[\alpha]_D$ −49° (*c*, 1·06) (Found: C, 87·95; H, 12·35. $C_{30}H_{50}$ requires C, 87·75; H, 12·25%).

Ozonolysis of γ-Butyrospermadiene (IX).—γ-Butyrospermadiene (204 mg.) in acetic acid (100 c.c.) was treated with ozonised oxygen for 15 min. at 20°. Water (100 c.c.) and ferrous sulphate (*ca.* 1·0 g.) were added and 80 c.c. of the mixture were distilled into a solution of 2 : 4-dinitrophenylhydrazine (500 mg.) in methanol (20 c.c.) containing concentrated sulphuric acid (2 c.c.). After dilution of the distillate with water (100 c.c.) extraction with benzene afforded a 2 : 4-dinitrophenylhydrazone which was adsorbed from dry benzene on alumina (20 g.). Elution with benzene (100 c.c.) gave a fraction (97 mg. ≡ 82% yield), m. p. 120—127°, which gave (from methanol) acetone 2 : 4-dinitrophenylhydrazone, m. p. 126—127°, undepressed on admixture with an authentic specimen (Found: N, 23·85. Calc. for $C_9H_{10}O_4N_4$: N, 23·55%).

Conversion of Dihydrobutyrospermyl Acetate into 7-Oxoeuph-8-enyl Acetate.—A solution of perbenzoic acid in chloroform (3·6%; 3 c.c.) was added to dihydrobutyrospermyl acetate (313 mg.) in chloroform (5 c.c.). After being kept at 20° for 72 hr. the mixture was worked up in the usual manner, yielding a gum (340 mg.) which was adsorbed from benzene on alumina (30 g.). Elution with benzene yielded a fraction (186 mg.) which was crystallised from methanol, giving 7-oxoeuph-8-en-3β-yl acetate as needles, m. p. 168—171°, undepressed on admixture with an authentic sample, $[\alpha]_D$ +35° (*c*, 0·53) (Found: C, 79·15; H, 11·5. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). Light absorption in ethanol: Max., 2550 Å; ε = 10,200.

Conversion of Dihydrobutyrospermyl Acetate into Eupha-7 : 9(11)-dienyl Acetate.—Dihydrobutyrospermyl acetate (365 mg.) in chloroform (6 c.c.) was treated with a 4% solution of perbenzoic acid in chloroform (2 c.c.), and the mixture kept for 3 days at 20°. After being washed with sodium hydroxide solution and water the solution was evaporated to give a gum which was adsorbed from benzene on alumina (activity II; 35 g.). Elution with benzene–ether (9 : 1) gave eupha-7 : 9(11)-dienyl acetate as needles, m. p. 107·5—110° (after several crystallisations from methanol–ethyl acetate), undepressed on admixture with an authentic sample $[\alpha]_D$ −94° (*c*, 1·01). Light absorption: Max., 2325 and 2395 Å, ε = 15,850 and 17,400; inflexion 2470 Å, ε = 11,500.

Catalytic Isomerisation of Dihydrobutyrospermyl Acetate.—Dihydrobutyrospermyl acetate (40 mg.) in acetic acid (20 c.c.) was shaken with a platinum catalyst (150 mg.) in an atmosphere of hydrogen. After filtration and dilution with water, ethereal extraction gave a product which was crystallised several times from ethanol to give euph-8-enyl acetate (dihydro*iso*-butyrospermyl acetate) as needles, m. p. 124—126°, undepressed on admixture with an authentic sample of euph-8-enyl acetate, depressed on admixture with dihydrobutyrospermyl acetate, $[\alpha]_D$ +33° (*c*, 1·24). The infrared spectrum of the product was identical with that of authentic euph-8-enyl acetate.

Conversion of Euphyl Acetate into iso*Butyrospermyl Acetate.*—Dry hydrogen chloride was passed through a solution of euphyl acetate (400 mg.) in chloroform (10 c.c.) at 0° for 2 hr. After removal of the solvent the product was heated under reflux in dimethylaniline (6 c.c.) for 2½ hr. After cooling and addition of light petroleum the dimethylaniline was removed by washing with dilute hydrochloric acid. The product was then isolated with light petroleum. It was crystallised four times from ethanol giving *iso*butyrospermyl acetate (eupha-8 : 25-dienyl

acetate) as needles, m. p. 104·5—106°, undepressed on admixture with *iso*butyrospermyl acetate, $[\alpha]_D$ +37° (*c*, 1·48). The infrared spectra of *iso*butyrospermyl acetate and of the product from euphyl acetate were identical.

7ξ-Deuteroeuph-8-enyl Acetate.—Dihydrobutyrospermyl acetate (325 mg.) was dissolved in dry alcohol-free chloroform (10 c.c.) and 2 drops of deuterium oxide were added. The solution was cooled to 0° and a stream of deuterium chloride was passed through it for 2½ hr., with intermittent shaking. After removal of the solvent, the product was crystallised, giving 7-deuteroeuph-8-enyl acetate as needles (from ethanol), m. p. 127—128·5°, $[\alpha]_D$ +34° (*c*, 1·62).

Oxidation of 7ξ-Deuteroeuph-8-enyl Acetate.—7ξ-Deuteroeuph-8-enyl acetate (1·7 g.) was oxidised with chromic acid in acetic acid in essentially the same manner as for euph-8-enyl acetate (see below). The oxidation product was adsorbed on alumina (170 g.) which was first eluted with light petroleum–benzene (1 : 1; 1 l.) and benzene (1·2 l.). Further elution with benzene (1100 c.c.) and benzene–ether (19 : 1; 750 c.c.) gave 7-oxoeuph-8-enyl acetate (115 mg.), m. p. 164—168° (from methanol), undepressed on admixture with an authentic sample. Light absorption: Max., 2545 Å; ε = 10,500. The absence of any light absorption at 2143 cm.$^{-1}$ (determined in carbon tetrachloride) showed that there was no deuterium in the compound.

Oxidation of Euph-8-enyl Acetate.—Euph-8-enyl acetate (2 g.) in acetic acid (90 c.c.) was treated dropwise at 20° with a solution of chromic acid in 90% acetic acid (9 c.c.; ≡ 2·25 atoms of oxygen per molecule of euph-8-enyl acetate). The mixture was kept at 50° for 4½ hr. After dilution with water, extraction with ether yielded a gum (2 g.) which was subjected to ultraviolet spectrographic analysis. This indicated the presence of 7-oxoeuph-8-enyl acetate (36%), 7 : 11-dioxoeuph-8-enyl acetate (30%), and eupha-7 : 9(11)-dienyl acetate (3%). The gum was adsorbed from light petroleum on alumina (200 g.). Benzene–light petroleum (1 : 1) eluted unchanged euph-8-enyl acetate (175 mg.). The 7 : 11-dioxo-derivative (580 mg.) was next eluted with benzene (900 c.c.), and then further elution with benzene (1400 c.c.) and benzene–ether (19 : 1; 500 c.c.) gave 7-oxoeuph-8-enyl acetate (435 mg.), m. p. 166—169° (from methanol).

Oxidation of Eupha-7 : 9(11)-dienyl Acetate.—Chromic acid in 90% acetic acid (0·87 c.c. ≡ 1 atom of oxygen per molecule of triterpene) was added dropwise to eupha-7 : 9(11)-dienyl acetate (460 mg.) in acetic acid (20 c.c.) at 20°. The mixture was then heated for 4 hr. at 50°. After dilution with water, extraction with ether yielded a yellow gum (440 mg.), whose ultraviolet spectrum indicated that it contained eupha-7 : 9(11)-dienyl acetate (45%), 7 : 11-dioxoeuph-8-enyl acetate (*ca.* 25%), and a trace of 7-oxoeuph-8-enyl acetate. The product was dissolved in dry ether (10 c.c.), boron trifluoride–ether (0·2 c.c.) was added, and the mixture was kept overnight at 20°. The solution was then worked up in the usual manner to give a yellow gum (430 mg.) whose ultraviolet absorption spectrum indicated that it contained eupha-7 : 9(11)-dienyl acetate (45%), 7 : 11-dioxoeuph-8-enyl acetate (28—30%), and 7-oxoeuph-8-enyl acetate (about 6%).

Zimmermann Test.—A solution of the requisite ketone in ethanol (0·2 c.c.; 0·15% w/v) was treated with alcoholic potassium hydroxide (0·2 c.c.; 14% w/v) and alcoholic *m*-dinitrobenzene (0·2 c.c.; 1·16% w/v), and the mixture was kept at 25° for either 5 or 60 min. It was then diluted to 10 c.c. with ethanol and its light absorption between 3000 and 6000 Å determined. A blank experiment was also carried out, the solution being used in the compensating cell of the spectrophotometer.

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