635. *Triterpenoids. Part LIII.* The Constitution and Stereochemistry of Butyrospermol.*

By WILLIAM LAWRIE, WILLIAM HAMILTON, F. S. SPRING, and H. S. WATSON.

Oxidation of dihydrobutyrospermyl acetate with chromic acid gives 7-oxo*apo*euphenyl acetate, which is isomerised by mineral acid to 7-oxo*iso*-euph-13(17)-enyl acetate (XIV). The latter is identified by its reduction, by the Wolff–Kishner method and reacetylation, to *iso*euph-13(17)-enyl acetate (VI), and by its oxidation with selenium dioxide to 7-oxo*iso*eupha-11 : 13(17)-dienyl acetate (XVI). Similar reduction of 7-oxo*apo*euphenyl acetate gives *apo*euphenyl acetate which is isomerised by hydrogen chloride to *iso*euph-13(17)-enyl acetate (VI); euph-8-enyl acetate is unchanged under the same acid treatment. Oxidation of 7-oxo*apo*euphenyl acetate with selenium dioxide gives an αβ-unsaturated ketone, 7-oxo*apo*euphadienyl acetate, which is isomerised by mineral acid to 7-oxo*iso*eupha-5 : 13(17)-dienyl acetate (XX). The formation of 7-oxo*apo*euphenyl acetate is shown to involve a molecular rearrangement, and of the two possible structures, (XII) and (XIII), for this compound the former is preferred. The conversion of dihydrobutyrospermyl acetate into 7-oxo*apo*euphenyl acetate (XII) proves that the double bond in the former is between $C_{(7)}$ and $C_{(8)}$. The methyl-group migration included in this conversion is considered to synchronise with oxidation at the 7 : 8-double bond and accordingly the reaction does not involve the $C_{(9)}$-hydrogen atom. It follows that the $C_{(9)}$-hydrogen atom in dihydrobutyrospermyl acetate has the same configuration (α) as that in *iso*euph-13(17)-enyl acetate, that the former compound is 9α-euph-7-en-3β-yl acetate (XI; R = Ac), and that butyrospermol is 9α-eupha-7 : 24-dien-3β-ol (XVII). Confirmation of structure (XVII) for butyrospermol is obtained from consideration of molecular-rotation relations. The euph-7-enyl acetate obtained by Wolff–Kishner reduction of 7-oxoeuph-8-enyl acetate, and reacetylation, is considered to be the 9β-epimer of dihydrobutyrospermyl acetate.

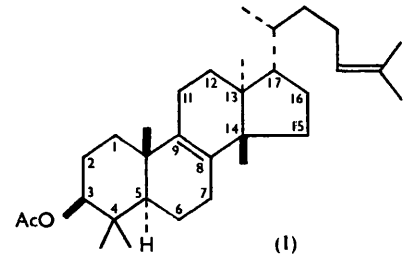
ADDITION of bromine to the side-chain double bond in butyrospermyl acetate, followed by isomerisation of the nuclear double bond with hydrogen chloride at 0°, and regeneration of the side-chain double bond with zinc, gives eupha-8 : 24-dienyl acetate (euphyl acetate) (I). Oxidation of dihydrobutyrospermyl acetate with osmic acid and acetylation of the product gives a saturated triol diacetate which is converted into eupha-7 : 9(11)-dienyl acetate (II) by mild heat. These observations led Irvine, Lawrie, McNab, and Spring [1,2] to the view that butyrospermol is either 9ξ-eupha-7 : 24-dien-3β-ol (III) or 8ξ-eupha-9(11) : 24-dien-3β-ol (IV). A similar decision has been reached by Jones and his collaborators [3,4] who, however, preferred the 9β-formulation of (III). The present paper describes experiments which show that butyrospermol is 9α-eupha-7 : 24-dien-3β-ol (XVII).

Oxidation of dihydrobutyrospermyl acetate, $C_{32}H_{54}O_2$, with chromic acid at 16° gives a mixture, chromatography of which yields an acetate, $C_{32}H_{52}O_3$, in approximately 25% conversion yield. This acetate is unchanged after being heated with pyridine and acetic anhydride and is stable to chromic–acetic acid at room temperature. It contains an isolated ethylene bond, since it gives a yellow colour with tetranitromethane, and shows absorption between 2000 and 2200 Å. The presence of an isolated keto-group in a six-membered ring in the acetate, $C_{32}H_{52}O_3$, is inferred from its infrared absorption spectrum (in carbon tetrachloride) which contains a strong band at 1710 cm.$^{-1}$ in addition to one at

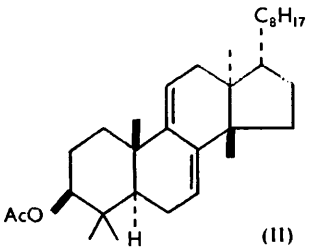
* Part LII, *J.*, 1956, 2419.

[1] Irvine, Lawrie, McNab, and Spring, *Chem. and Ind.*, 1955, 626.
[2] *Idem*, *J.*, 1956, 2029.
[3] Dawson, Halsall, Jones, Meakins, and Phillips, *Chem. and Ind.*, 1955, 918.
[4] Jones and Halsall, "Fortschritte der Chemie organischer Naturstoffe," Springer-Verlag, 1955, Vol. XII, p. 108.

1735 cm.$^{-1}$ (acetate). The presence of a keto-group is also established by reactions described later. This non-conjugated unsaturated oxo-acetate which we name oxo*apo*euphenyl acetate, is not isomerised to an αβ-unsaturated ketone by treatment with either alkali or mineral acid. After treatment with alkali and reacetylation of the product, oxo*apo*euphenyl acetate is recovered. Hydrochloric–acetic acid converts oxo*apo*euphenyl



(I)



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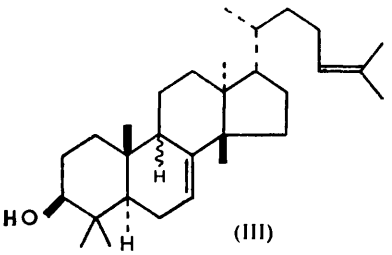

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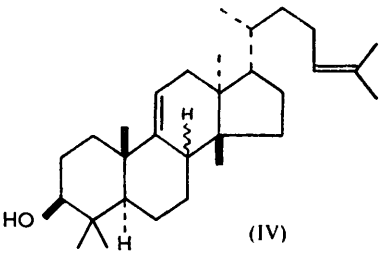

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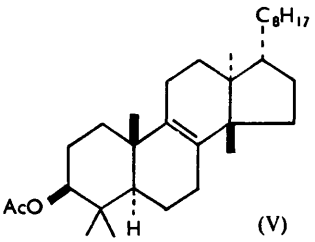

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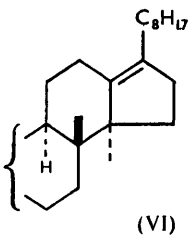

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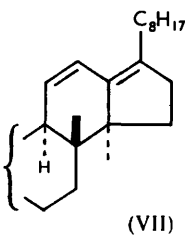

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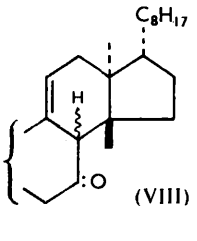

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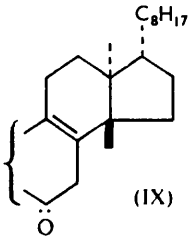

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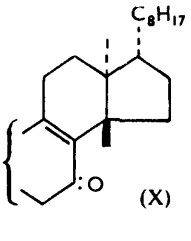


(X)

acetate into an isomeric non-conjugated unsaturated ketone, reduction of which, by the forcing variant of the Wolff–Kishner method,[5] followed by acetylation, gives *iso*euph-13(17)-enyl acetate (VI), identical with the product obtained by mineral-acid rearrangement of euph-8-enyl acetate (V).[6–8] The isomeric non-conjugated unsaturated ketone is thus

[5] Barton, Ives, and Thomas, *J.*, 1955, 2056.
[6] Vilkas, Dupont, and Dulou, *Bull. Soc. chim. France*, 1949, **16**, 813.
[7] Barton, McGhie, Pradhan, and Knight, *J.*, 1955, 876.
[8] Arigoni, Viterbo, Dünnenberger, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1954, **37**, 2306; Ménard, Wyler, Hiestand, Arigoni, Jeger, and Ruzicka, *ibid.*, 1955, **38**, 1517.

an oxo*iso*euph-13(17)-enyl acetate in which the carbonyl oxygen is not attached to $C_{(12)}$. Oxidation of oxo*iso*euph-13(17)-enyl acetate with selenium dioxide gives an oxo*iso*eupha-11 : 13(17)-dienyl acetate which shows the same characteristic ultraviolet absorption spectrum as *iso*eupha-11 : 13(17)-dienyl acetate (VII), obtained by oxidation of *iso*euph-13(17)-enyl acetate (VI) with selenium dioxide.[7] The formation of oxo*iso*eupha-11 : 13(17)-dienyl acetate shows that the keto-group in oxo*iso*euph-13(17)-enyl acetate, and in oxo*apo*euphenyl acetate, does not include $C_{(11)}$ or $C_{(12)}$; consequently, this group is at $C_{(6)}$ or $C_{(7)}$.

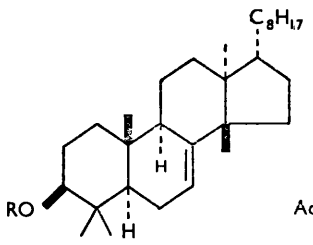
If oxo*apo*euphenyl acetate is derived from dihydrobutyrospermyl acetate without molecular rearrangement, it is either (VIII) or (IX). The formation of the ketone (VIII) from a euph-7-enyl acetate or from a euph-9(11)-enyl acetate would require the mediation of eupha-7 : 9(11)-dienyl acetate (II),[9,10] since a double bond will not move out of conjugation with a carbonyl group under the conditions used for the preparation of oxo*apo*euphenyl acetate, and more particularly 7-oxoeuph-8-enyl acetate (X) [7,11,12] is stable to mineral acid. Under the conditions used for the oxidation of dihydrobutyrospermyl acetate to oxo*apo*euphenyl acetate, eupha-7 : 9(11)-dienyl acetate is oxidised by chromic acid to a mixture, chromatography of which failed to disclose the presence of the non-conjugated unsaturated ketone, so establishing that the 7 : 9(11)-dienyl acetate (II) is not an intermediate in the oxidation of dihydrobutyrospermyl acetate to oxo*apo*euphenyl acetate, and that the latter is not 7-oxoeuph-9(11)-enyl acetate (VIII). This decision, together with the exclusion of formulæ for oxo*apo*euphenyl acetate in which the carbonyl group is at $C_{(11)}$ or $C_{(12)}$, shows that butyrospermol cannot be a eupha-9(11) : 24-dienol (IV), and it is thus identified as a eupha-7 : 24-dienol (III) in which only the configuration at $C_{(9)}$ remains to be determined. Under the conditions used for the oxidation of dihydrobutyrospermyl acetate to oxo*apo*euphenyl acetate, euph-8-enyl acetate gives a mixture, chromatography of which failed to disclose the presence of a trace of oxo*apo*euphenyl acetate. This shows that the latter compound is not formed from dihydrobutyrospermyl acetate *via* euph-8-enyl acetate.

Formula (IX) cannot represent oxo*apo*euphenyl acetate for the following reasons: The infrared absorption spectrum of the unsaturated ketone includes a band at 1640 $cm.^{-1}$ attributed to a double bond which is not fully substituted. Wolff–Kishner reduction of oxo*apo*euphenyl acetate, followed by acetylation of the product, gives *apo*euphenyl acetate, which is different from euph-8-enyl acetate (V) and from dihydrobutyrospermyl acetate. The ultraviolet absorption of *apo*euphenyl acetate shows that its double bond is at least trisubstituted. The decision that oxo*apo*euphenyl acetate is neither (VIII) nor (IX) is supported by the observation, recorded earlier, that oxo*apo*euphenyl acetate is not isomerised to an αβ-unsaturated ketone by treatment with either alkali or mineral acid.

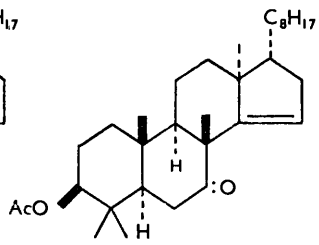
These considerations show that the formation of oxo*apo*euphenyl acetate from dihydrobutyrospermyl acetate has included a molecular rearrangement, and support for this decision was obtained from an examination of *apo*euphenyl acetate. Treatment of this acetate with hydrogen chloride in chloroform at 0° for 2 hours converts it into *iso*euph-13(17)-enyl acetate (VI). After the same treatment euph-8-enyl acetate (V) is unchanged and dihydrobutyrospermyl acetate is simply isomerised to euph-8-enyl acetate (V).[1,2] We represent the formation of oxo*apo*euphenyl acetate from dihydrobutyrospermyl acetate (a euph-7-enyl acetate) as a synchronous reaction in which oxidation at the 7 : 8-double bond is accompanied by movement of the $C_{(14)}$-methyl group to $C_{(8)}$. Two paths whereby the initiated reaction proceeds are to be considered. First, the movement of the $C_{(14)}$-methyl group to $C_{(8)}$ is accompanied by, and the path terminates in, the loss of a proton from $C_{(15)}$. Following the second, the migration of the 14β-methyl group to $C_{(8)}$ is accompanied by migration of the 13α-methyl group to $C_{(14)}$ and loss of the 12β-hydrogen as a proton. Whichever path is followed, the carbonyl group in oxo*apo*euphenyl acetate is at $C_{(7)}$, and according to the first mechanism 7-oxo*apo*euphenyl acetate is (XII) and its conversion into 7-oxo*iso*euph-13(17)-enyl acetate (XIV), by treatment with mineral acid,

[9] Barbour, Bennett, and Warren, *J.*, 1951, 2540.
[10] Dawson, Halsall, and Swayne, *J.*, 1953, 590.
[11] McDonald, Warren, and Williams, *J.*, 1949, S155.
[12] Vilkas, *Bull. Soc. chim. France*, 1950, **17**, 582.

involves protonation of the 14 : 15-double bond, simultaneous movement of the 13α-methyl group to $C_{(14)}$ and loss of the 17β-hydrogen as a proton. If the second path is followed, 7-oxo*apo*euphenyl acetate is (XIII) and its subsequent isomerisation to 7-oxo*iso*-euph-13(17)-enyl acetate (XIV) is a simple carbonium-ion induced movement of the double bond from the 12- to the 13(17)-position. The oxo-dienyl acetate obtained by oxidation of 7-oxo*iso*euph-13(17)-enyl acetate (XIV) with selenium dioxide is represented as 7-oxo*iso*eupha-11 : 13(17)-dienyl acetate (XVI). A fundament of these mechanisms is that the $C_{(9)}$-hydrogen in dihydrobutyrospermyl acetate is not involved in the oxidation of this acetate to 7-oxo*apo*euphenyl acetate, *i.e.*, that the orientation of the $C_{(9)}$-hydrogen in dihydrobutyrospermyl acetate is the same (α) as that in 7-oxo*iso*euph-13(17)-enyl acetate (XIV). Accordingly we represent dihydrobutyrospermyl acetate as 9α-euph-7-en-3β-yl acetate (XI; R = Ac) and butyrospermol as 9α-euph-7 : 24-dien-3β-ol (XVII).



(XI)



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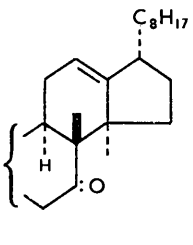

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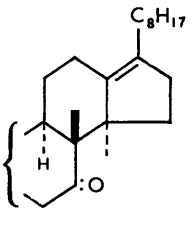
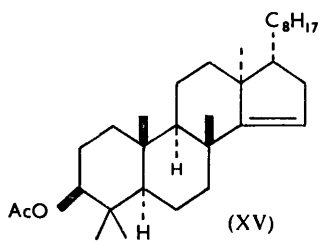
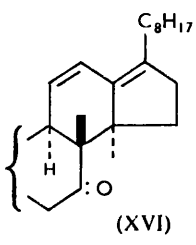


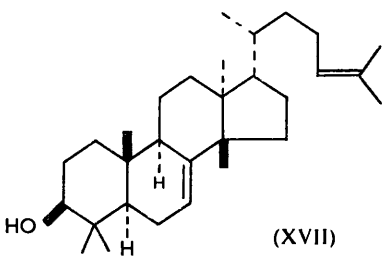
(XIV)



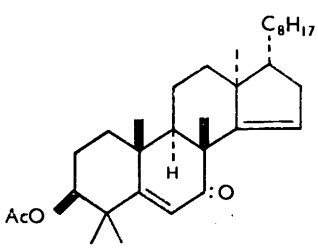
(XV)



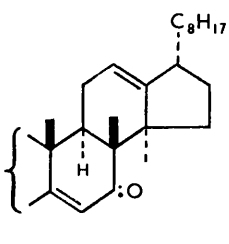
(XVI)



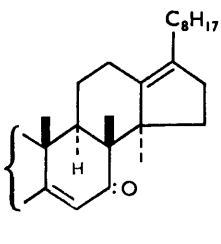
(XVII)



(XVIII)



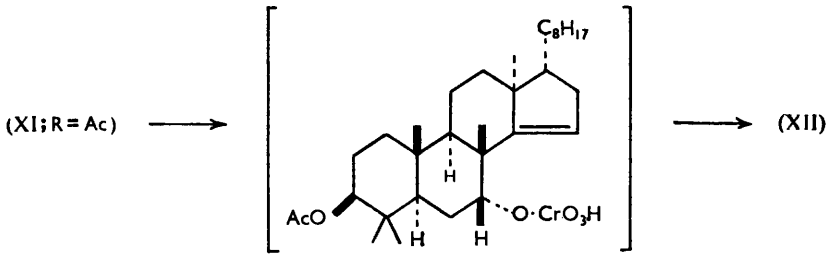
(XIX)



(XX)

Although a decision between formulæ (XII) and (XIII) for 7-oxo*apo*euphenyl acetate is not pertinent to our argument concerning the structure and stereochemistry of butyrospermol, we favour the former alternative for the reasons discussed below. Oxidation of 7-oxo*apo*euphenyl acetate with selenium dioxide gives an αβ-unsaturated ketone, $C_{32}H_{50}O_3$, which shows an ultraviolet absorption maximum at 2350 Å (ε = 14,000) together with strong absorption in the ethylenic region. It gives a yellow colour with tetranitromethane and its infrared absorption spectrum, in Nujol, includes bands at 1735, 1240 (acetate), 1660 (αβ-unsaturated ketone), and 1634 $cm.^{-1}$ (isolated double bond). The oxidation of oxo*apo*euphenyl acetate with selenium dioxide has thus resulted in the introduction of a double bond in the 5 : 6-position, and the product is either (XVIII) or (XIX). Treatment

of the αβ-unsaturated oxo-acetate, $C_{32}H_{50}O_3$, with mineral acid converts it into an isomer which also shows the characteristic absorption spectrum of an αβ-unsaturated ketone ($\lambda_{max.}$ 2380 Å; $\varepsilon = 15{,}000$) together with strong absorption in the ethylenic region of the spectrum. This isomer is formed from the αβ-unsaturated ketone, (XVIII) or (XIX), by a mechanism similar to that operating the conversion of 7-oxo*apo*euphenyl acetate, (XII) or (XIII), into 7-oxo*iso*euph-13(17)-enyl acetate (XIV), and it is considered to be 7-oxo*iso*eupha-5 : 13(17)-dienyl acetate (XX). The fact that the double bond in 7-oxo*apo*-euphenyl acetate is not attacked by selenium dioxide, supports the view that this compound is (XII) and not (XIII). This is also supported by the stability of the double bond in 7-oxo*apo*euphenyl acetate towards chromic acid which, if 7-oxo*apo*euphenyl acetate is (XIII), is difficult to reconcile with the ease with which the analogously constituted α-amyrin acetate and β-amyrin acetate are attacked by this oxidising agent. The product obtained by Wolff–Kishner reduction of 7-oxo*apo*euph-14-enyl acetate (XII) is formulated as (XV), and its acid-induced isomerisation to *iso*euph-13(17)-enyl acetate (VI) involves protonation of the double bond accompanied by movement of the 13α-methyl group to $C_{(14)}$ and loss of the 17β-hydrogen atom. The formation of 7-oxo*apo*euph-14-enyl acetate from dihydrobutyrospermyl acetate (XI; R = Ac) is represented as attack at the double bond from the rear (α), as illustrated.

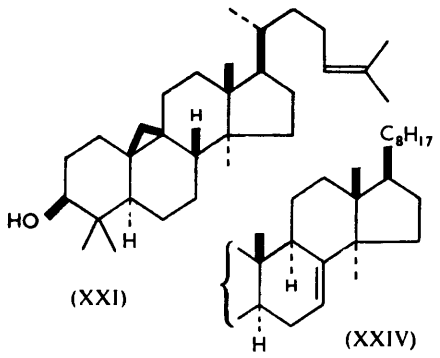


In an attempt to prepare 7-oxo*apo*euph-14-enyl acetate by another method, dihydrobutyrospermyl acetate was treated with ozone. The product, $C_{32}H_{54}O_3$, did not give a colour with tetranitromethane and did not show selective absorption in the ultraviolet region. It was identified as dihydrobutyrospermyl acetate oxide by treatment with hydrogen chloride which gave eupha-7 : 9(11)-dienyl acetate (II) in high yield. The epoxide and chromic acid–acetic acid give a mixture which does not contain 7-oxo*apo*-euph-14-enyl acetate.

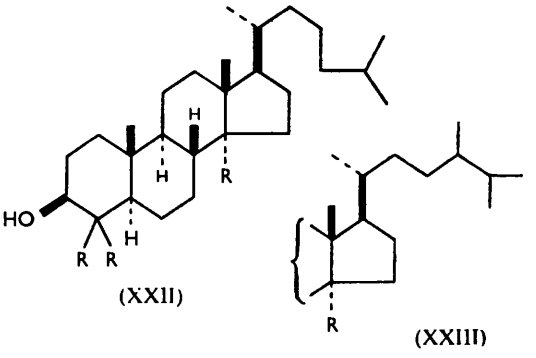
Barton [13] noted that the change in molecular rotation (Δ_3) on oxidation of butyrospermol and *cyclo*artenol to the corresponding ketones is in each case negative, an unusual feature in triterpenoid compounds, and for this reason he suggested that the two alcohols may be related. The constitution and stereochemistry of *cyclo*artenol have subsequently been shown to be represented by (XXI) [14–16] and Jones and his collaborators [3,4] have suggested that the similarity in the Δ_3 values is explained if butyrospermol, like *cyclo*-artenol, has a 9β-substituent, and they have tentatively formulated butyrospermol as 9β-eupha-7 : 24-dien-3β-ol. We believe that this argument is invalid. A widely accepted principle in the application of molecular rotation relations to structure analysis is that terminal rings of the same type make contributions to the molecular rotation which are very approximately independent of the rest of the molecule, provided that the adjacent ring is a saturated unsubstituted *cyclo*hexane ring.[17,18] Another generally accepted principle is that nonangular methyl groups have little effect on the contribution of a terminal ring to the molecular rotation. Thus the change in molecular rotation (Δ_{CO})

[13] Barton, *J.*, 1951, 1444.
[14] Bentley, Henry, Irvine, and Spring, *J.*, 1953, 3673.
[15] Barton, Page, and Warnhoff, *J.*, 1954, 2715.
[16] Irvine, Henry, and Spring, *J.*, 1955, 1316.
[17] Klyne, *J.*, 1952, 2916.
[18] Mills and Klyne in " Progress in Stereochemistry," Butterworths, London, Vol. I, p. 177.

consequent upon the introduction of a 3-carbonyl oxygen into many 5α-steroid and triterpenoid hydrocarbons is positive and the molecular-rotation change (Δ_3) accompanying the oxidation of a 3β-hydroxy-5α-steroid or of a 3β-hydroxy-triterpenoid to the corresponding ketone is also positive. Data illustrating these principles have been assembled



(XXI) (XXIV)



(XXII) (XXIII)

by Klyne.[17] We draw attention to two exceptions. The change in rotation when lanostanol (XXII; R = Me) and laudanol (XXIII; R = Me) are oxidised to the corresponding ketones is in each case *negative* and the change accompanying the conversion of lanostane and laudane into the corresponding 3-ketones is in each case *negative*. In Table 1, molecular-

TABLE 1.

	M_D				
	3β-Alcohol	Hydrocarbon	3-Ketone	Δ_3	Δ_{CO}
Lanostanol (XXII; R = Me) [a]	+150°	+149°	+116°	−34°	−33°
Laudanol (XXIII; R = Me) [b]	+ 93	+107	+ 62	−31	−45
Cholestanol (XXII; R = H) [c]	+ 93	+ 91	+159	+66	+68
Ergostanol (XXIII; R = H) [d]	+ 64	+ 66	+140	+76	+74

[a] From Voser, Montavon, Günthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893. [b] From Bentley, Henry, Irvine, Mukerji, and Spring, *J.*, 1955, 596. [c] From Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold, 1949. [d] From Reindel and Walter, *Annalen*, 1928, **460**, 212; Reindel, Walter, and Rauch, *ibid.*, 1927, **452**, 34.

rotation changes for lanostanol (XXII; R = Me) and laudanol (XXIII; R = Me) are compared with corresponding changes for cholestanol (XXII; R = H) and ergostanol (XXIII; R = H). These data show that the introduction of methyl groups at $C_{(4)}$ and $C_{(14)}$ has a substantial effect upon the molecular-rotation contribution of the terminal rings in both cholestanol and ergostanol. The recognition of this effect led us to compare the molecular-rotation changes associated with reactions of dihydrobutyrospermol (XI; R = H) with corresponding changes for lanost-7-en-3β-ol (XXIV). The molecular rotations are shown in Table 2. The change in molecular rotation occurring when lanost-

TABLE 2.

	M_D						
	Alcohol	Acetate	Benzoate	Ketone	Δ_1	Δ_2	Δ_3
Lanost-7-en-3β-ol (XXIV) [a]	+45°	+156°	+266°	− 85°	+111°	+221°	−130°
Dihydrobutyrospermol (XI; R = H) [b]	−60	+ 56	+164	−182	+116	+224	−122

[a] From this paper. [b] From Heilbron, Jones, and Robins, *J.*, 1949, 444.

7-en-3β-ol is oxidised to lanost-7-en-3-one is *negative* and almost identical with that associated with the oxidation of dihydrobutyrospermol and butyrospermol to the corresponding 3-ketones. Moreover the Δ_1 (acetylation) and Δ_2 (benzoylation) values for lanost-7-en-3β-ol are nearly identical with the related values for dihydrobutyrospermol. This close correspondence supports the proposed steric formula (XVII) for butyrospermol.

We next consider the euph-7-enyl acetate obtained by Wolff–Kishner reduction of

7-oxoeuph-8-enyl acetate followed by acetylation of the product.[7] This preparative method establishes that this acetate has the more stable configuration at $C_{(9)}$ which must be β since the stereochemistry of 9α-euph-7-enyl acetate (dihydrobutyrospermyl acetate) (XI; R = Ac) constrains the molecule to adopt a conformation which includes a boat, whereas 9β-euph-7-enyl acetate can assume an all-chair (or half-chair) conformation. We find that 9β-euph-7-enyl acetate is unchanged by treatment with hydrogen chloride under conditions which convert 9α-euph-7-enyl acetate (dihydrobutyrospermyl acetate) (XI; R = Ac) into euph-8-enyl acetate (V). We suggest that the strained conformation of 9α-euph-7-enyl acetate (XI; R = Ac) is the driving force of its irreversible conversion into euph-8-enyl acetate (V) which can adopt an all-chair (or half-chair) conformation.

Experimental

Specific rotations are for chloroform solutions at room temperature. Ultraviolet absorption spectra were measured in ethanol. Grade II alumina and light petroleum (b. p. 60—80°) were used for chromatography.

Dihydrobutyrospermyl Acetate Oxide.—Dihydrobutyrospermyl acetate (250 mg.) in ethyl acetate (60 c.c.) was treated at −30° with ozonised oxygen for 1 hr. The product was isolated in the usual way and crystallised from methanol, giving *dihydrobutyrospermyl acetate oxide* (160 mg.) as plates, m. p. 154—155°, $[\alpha]_D$ −21·5° (*c* 1·0 in benzene) (Found: C, 78·8; H, 11·2. $C_{32}H_{54}O_3$ requires C, 79·0; H, 11·2%). The oxide does not show selective absorption between 2000 and 3000 Å. It does not give a colour with tetranitromethane in ethyl acetate, but its solution in chloroform containing this reagent gradually becomes deep yellow.

Eupha-7 : 9(11)-dienyl Acetate from Dihydrobutyrospermyl Acetate Oxide.—The oxide (35 mg.) in chloroform (5 c.c.) was treated with dry hydrogen chloride for 2 hr. The product was isolated in the usual way and its solution in light petroleum (25 c.c.) chromatographed on alumina (3 g.). Elution with light petroleum (50 c.c.) gave a fraction (23 mg.) which crystallised from methanol to give eupha-7 : 9(11)-dienyl acetate as needles, m. p. and mixed m. p. 110—111°, $\lambda_{max.}$ 2320, 2400, and 2470 Å (ε 16,000, 18,000, and 11,000).

7-*Oxo*apo*euph*-14-*enyl Acetate* (XII).—Dihydrobutyrospermyl acetate (2 g.) in methylene chloride (20 c.c.) and acetic acid (250 c.c.) was treated dropwise during 30 min. at room temperature with chromium trioxide (844 mg.) in acetic acid (70 c.c.). The mixture was kept at room temperature for 16 hr., a little methanol then added, and the mixture evaporated to dryness under reduced pressure. The gum, isolated with ether, was chromatographed in light petroleum (100 c.c.) on alumina (60 g.). Elution with light petroleum (1200 c.c.) gave fractions (total 442 mg.) which yielded dihydrobutyrospermyl acetate as prismatic needles (from chloroform–methanol), m. p. and mixed m. p. 134—135°. Elution with light petroleum–benzene (9 : 1, 1350 c.c.; then 4 : 1, 750 c.c.) gave fractions (450 mg.) each of which showed selective absorption between 2500 and 2700 Å. Crystallisation of these fractions gave (with large loss) 7-oxoeuph-8-enyl acetate as needles, m. p. and mixed m. p. 162—163°, $[\alpha]_D$ +40° ± 5° (*c* 0·4). Continued elution with light petroleum–benzene (1 : 1; 1500 c.c.) gave fractions (335 mg.), which crystallised from methanol to give 7-*oxo*apo*euph*-14-*enyl acetate* as stout needles, m. p. 119—120°, $[\alpha]_D$ −85° (*c* 1·0), ε_{2100} = 5400 (Found: C, 79·2; H, 11·1. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). It gives a yellow colour with tetranitromethane and it is unchanged after treatment with acetic anhydride and pyridine at 100° for 1 hr. 7-Oxo*apo*euph-14-enyl acetate (100 mg.) in methylene chloride (1 c.c.)–acetic acid (30 c.c.) was treated dropwise during 15 min. with chromium trioxide (15 mg.) in acetic acid (3 c.c.), and the mixture kept at 20—25° for 24 hr. The chromium trioxide was not reduced and 7-oxo*apo*euph-14-enyl acetate, m. p. and mixed m. p. 118—120°, was recovered from the solution.

A solution of 7-oxo*apo*euph-14-enyl acetate (30 mg.) in 3% methanolic potassium hydroxide (10 c.c.) was refluxed for 2 hr. The hydrolysis product was isolated in the usual way and acetylated with acetic anhydride and pyridine for 1 hr. at 100°. The acetate was crystallised from methanol, yielding 7-oxo*apo*euph-14-enyl acetate (28 mg.) as needles, m. p. and mixed m. p. 119—120°.

7-*Oxo*iso*euph*-13(17)-*enyl Acetate* (XIV).—7-Oxo*apo*euph-14-enyl acetate (20 mg.) in concentrated hydrochloric acid–acetic acid (1 : 20; 2 c.c.) was kept at 100° for 3 hr. The product was isolated by means of ether and crystallised from methanol, yielding 7-*oxo*iso*euph*-13(17)-*enyl acetate* as plates, m. p. 112—113°, $[\alpha]_D$ −50° (*c* 1·3), ε_{2100} = 6700 (Found: 79·6; H, 11·0. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·8%). A mixture with 7-oxo*apo*euph-14-enyl acetate (m. p. 118—120°) had m. p. 93—105°. It gives a yellow colour with tetranitromethane in chloroform.

iso*Euph*-13(17)-*enyl Acetate* (VI) *from* 7-*Oxo*iso*euph*-13(17)-*enyl Acetate* (XIV).—The oxo-acetate (90 mg.) in diethylene glycol (10 c.c.) was mixed with a solution obtained by reaction of sodium (250 mg.) with diethylene glycol (15 c.c.), and the mixture heated to 200°. Anhydrous hydrazine was distilled in until the mixture refluxed at 180°. After refluxing for 18 hr. at 180°, the mixture was distilled until the temperature reached 210°, and refluxing was then continued for 24 hr. The product was isolated by means of ether, and acetylated by using acetic anhydride and pyridine at 100°. A solution of the dry acetylated product in light petroleum (25 c.c.) was chromatographed on alumina (5 g.). Elution with light petroleum (175 c.c.) gave a crystalline fraction (37 mg.) recrystallisation of which from methanol gave *iso*euph-13(17)-enyl acetate as plates, m. p. and mixed m. p. 110°, $[\alpha]_D$ −9° (*c* 2·0) (Found: C, 81·7; H, 11·7. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%).

7-*Oxo*iso*eupha*-11 : 13(17)-*dienyl Acetate* (XVI) *from* 7-*Oxo*iso*euph*-13(17)-*enyl Acetate* (XIV).—To a solution of 7-oxo*iso*euph-13(17)-enyl acetate (140 mg.) in acetic acid (14 c.c.) was added selenium dioxide (80 mg.) dissolved in the minimum of water, and the mixture was refluxed for 3 hr. The product was isolated by means of ether and its solution in light petroleum (300 c.c.) chromatographed on alumina (6 g.). Elution with light petroleum–benzene (4 : 1; 350 c.c.) gave fractions (32 mg.) which were crystallised twice from methanol, giving 7-*oxo*iso*eupha*-11 : 13(17)-*dienyl acetate* as plates, m. p. 107—109°, $[\alpha]_D$ −44·5° ± 5° (*c* 0·2), $\lambda_{max.}$ 2470, 2550, and 2640 Å (ε 19,000, 21,000, and 14,500) (Found: C, 79·4; H, 10·45. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It gives a deep brown colour with tetranitromethane in chloroform.

apo*Euph*-14-*enyl Acetate* (XV).—7-Oxo*apo*euph-14-enyl acetate (125 mg.) was reduced by using the forcing Wolff–Kishner method described above. The product was isolated and acetylated by using standard procedures, and a solution of the dry acetylated product (130 mg.) in light petroleum (50 c.c.) chromatographed on alumina (4 g.). Elution with light petroleum (150 c.c.) gave a fraction (74 mg.) which, when crystallised twice from methanol, gave apo*euph*-14-*enyl acetate* as needles, m. p. 114—115°, $[\alpha]_D$ −12° (*c* 1·1), ε_{2100} = 5300 (Found: C, 81·5; H, 11·7. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). A mixture with *iso*euph-13(17)-enyl acetate had m. p. 85—90°.

iso*Euph*-13(17)-*enyl Acetate* (VI) *from* apo*Euph*-14-*enyl Acetate* (XV).—*apo*Euph-14-enyl acetate (14 mg.) in dry chloroform (3 c.c.) was treated at 0° with a stream of dry hydrogen chloride for 2 hr. The product was isolated in the usual way and its solution in light petroleum (20 c.c.) filtered through alumina (3 g.). Light petroleum (200 c.c.) eluted a fraction (11·6 mg.) which crystallised from methanol to yield *iso*euph-13(17)-enyl acetate as plates, m. p. and mixed m. p. 109—110°, $[\alpha]_D$ −10° (*c* 0·4). A mixture with *apo*euph-14-enyl acetate (m. p. 114—115°) had m. p. 88—102°.

7-*Oxo*apo*eupha*-5 : 14-*dienyl Acetate* (XVIII).—A boiling solution of 7-oxo*apo*euph-14-enyl acetate (118 mg.) in acetic acid (4·8 c.c.) was treated dropwise with a solution of selenium dioxide (60 mg.) in the minimum of water and acetic acid (2 c.c.). The mixture was refluxed for 2 hr., the product isolated in the usual way, and its solution in light petroleum (25 c.c.) chromatographed on alumina (4 g.). The fractions (102 mg.), eluted with light petroleum (450 c.c.) and light petroleum–benzene (4 : 1; 200 c.c.), crystallised from methanol to give 7-*oxo*apo-*eupha*-5 : 14-*dienyl acetate* as prisms, m. p. 103—104°, $[\alpha]_D$ −126° (*c* 1·2), $\lambda_{max.}$ 2350 Å ($\varepsilon_{max.}$ 14,100, ε_{2100} = 9000) (Found: C, 79·4; H, 10·4. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%). It gives a yellow colour with tetranitromethane.

7-*Oxo*iso*eupha*-5 : 13(17)-*dienyl Acetate* (XX).—7-Oxo*apo*eupha-5 : 14-dienyl acetate (217 mg.) in concentrated hydrochloric–acetic acid (1 : 20; 10 c.c.) was kept at 100° for 2 hr. The product (212 mg.), in light petroleum (25 c.c.), was chromatographed on alumina (4 g.). Elution with light petroleum and mixtures of light petroleum with up to 50% benzene gave fractions (158 mg.) which crystallised from methanol to give 7-*oxo*iso*eupha*-5 : 13(17)-*dienyl acetate* (105 mg.) as prisms, m. p. 119—120°, $[\alpha]_D$ −52° (*c* 2·1), $\lambda_{max.}$ 2080 and 2380 Å (ε 10,400 and 13,500) (Found: C, 79·3; H, 10·3. $C_{32}H_{50}O_3$ requires C, 79·6; H, 10·4%).

Lanost-7-enyl Acetate.—This was prepared by the method of Marker, Wittle, and Mixon;[19] it separates from methanol–ethyl acetate as plates, m. p. 144—145°, $[\alpha]_D$ +33·2° (*c* 2·6). Barton, Fawcett, and Thomas[20] give m. p. 145°, $[\alpha]_D$ +32°. Hydrolysis of the acetate, with lithium aluminium hydride, gave lanost-7-en-3β-ol (XXIV) as needles (from methanol–ethyl acetate), m. p. 157—158°, $[\alpha]_D$ +10·4° (*c* 1·5). Woodward *et al.*[21] give m. p. 162—163°, $[\alpha]_D$ +10°. Lanost-7-enyl benzoate was prepared from the alcohol in the usual way; it separates from

[19] Marker, Wittle, and Mixon, *J. Amer. Chem. Soc.*, 1937, **59**, 1368.
[20] Barton, Fawcett, and Thomas, *J.*, 1951, 3147.
[21] Woodward, Patchett, Barton, Ives, and Kelly, *J. Amer. Chem. Soc.*, 1954, **76**, 2852.

methanol as needles, m. p. 207—209°, $[\alpha]_D$ +50° (*c* 1·9). Woodward *et al.*[21] give m. p. 207—208°, $[\alpha]_D$ +51°.

Lanost-7-en-3-one.—A solution of lanost-7-en-3β-ol (2 g.) in pyridine (40 c.c.) was kept for 24 hr. at 16° with the complex prepared from chromium trioxide (2 g.) and pyridine (20 c.c.). The product was isolated in the usual way and crystallised from methanol–ether, giving lanost-7-en-3-one as blades, m. p. 146—147°, $[\alpha]_D$ −20° (*c* 2·8) (Found : C, 84·7; H, 12·0. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). Marker *et al.*[19] give m. p. 149°.

Ozonolysis of Euph-8-enyl Acetate.—Euph-8-enyl acetate (10·0 g.) in ethyl acetate (300 c.c.) was treated with a slow stream of ozone at −5° for 2 hr. After the solution had been washed with aqueous ferrous sulphate and sodium hydrogen carbonate solutions, the solvent was removed under reduced pressure and the product chromatographed on alumina (330 g.). Elution with light petroleum–benzene (1 : 1; 3·2 l.) and crystallisation from methanol gave crystals (490 mg.) repeated crystallisation of which yielded 11-oxoeuph-8-enyl acetate (128 mg.) as blades, m. p. and mixed m. p. 127—128°, $[\alpha]_D$ +26·2° (*c* 2·2), $\lambda_{max.}$ 2570 Å (log ε 3·93). Barton *et al.*[7] give m. p. 130—131°, $[\alpha]_D$ +28°, $\lambda_{max.}$ 2550 Å (log ε 3·99). Elution of the column with benzene–light petroleum (3 : 1, 4 l.) and benzene (4·8 l.), and four crystallisations from methanol gave 7-oxoeuph-8-enyl acetate (716 mg.) as needles, m. p. 163—165°, $[\alpha]_D$ +35·5° (*c* 1·4), $\lambda_{max.}$ 2540 Å (log ε 4·0).

9β-*Euph-7-enyl Acetate.*—7-Oxoeuph-8-enyl acetate (690 mg.) was reduced by using forcing Wolff–Kishner conditions as described by Barton *et al.*[7] The dry acetylated product in light petroleum was chromatographed on alumina (22 g.). Light petroleum (650 c.c.) eluted a fraction, crystallisation of which from acetone–methanol gave 9β-euph-7-enyl acetate (160 mg.) as blades, m. p. 78—79°, $[\alpha]_D$ −98° (*c* 0·4), $\varepsilon_{2060} = 3060$ (Found : C, 81·3; H, 11·5. Calc. for $C_{32}H_{54}O_2$: C, 81·6; H, 11·6%). It gives a pale yellow colour with tetranitromethane. Barton *et al.*[7] give m. p. 92—94°, $[\alpha]_D$ −60°.

9β-Euph-7-enyl acetate (113 mg.) in chloroform (15 c.c.) was treated at 0° with dry hydrogen chloride for 2 hr. From the solution 9β-euph-7-enyl acetate was recovered in good yield as blades, m. p. 76—78° (no depression), $[\alpha]_D$ −95° (*c* 0·9).

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