as the parent hormone. It can be concluded, therefore, that isomerization at C-8 of progesterone does not result in any marked diminuition of hormonal activity.

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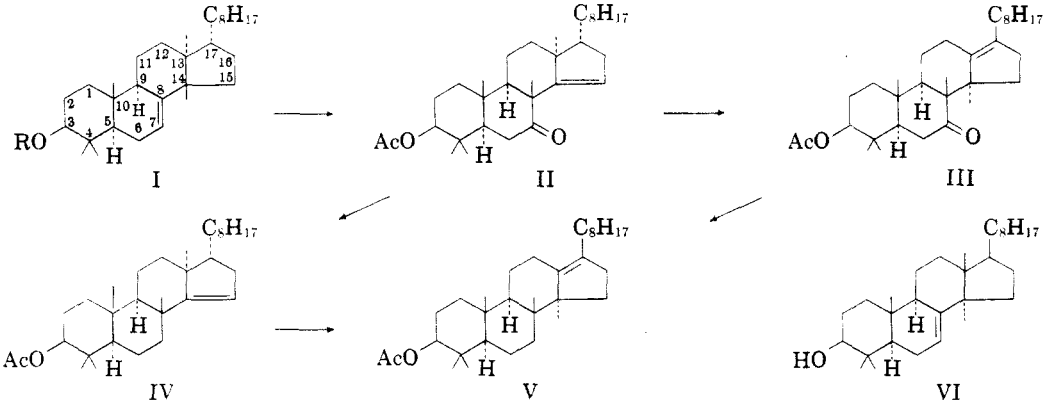
The Constitution of Butyrospermol

Sir:

A recent Communication[1] described the conversion of butyrospermol into euphol. Osmic acid converts dihydrobutyrospermyl acetate into a triol which forms a diacetate [m.p. 181–182°, $[\alpha]_D$ −82° (*c*, 1.2).[2] Found: C, 74.9; H, 10.9. $C_{34}H_{58}O_5$ requires C, 74.7; H, 10.7] and this on heating at 100° gives eupha-7:9(11)-dienyl acetate [m.p. and mixture m.p. 111–112°, $[\alpha]_D$ −78° (*c*, 1.0), $\lambda_{max.}$ 2320, 2400 (log. ϵ = 4.24) and 2470 Å.]. The less reactive double bond in butyrospermol is therefore trisubstituted and not tetrasubstituted[3] and this alcohol is either a 9ξ-eupha-7:24-dien-3β-ol or an 8ξ-eupha-9(11):24-dien-3β-ol.[1,4] We now wish to describe experiments which identify butyrospermol as 9α-eupha-7:24-dien-3β-ol.

Oxidation of dihydrobutyrospermyl acetate (I, R = Ac) with chromic acid yields 7-oxo*apo*euph-14-enyl acetate (II) [m.p. 119–120°, $[\alpha]_D$ −85° (*c*, 1.0), ϵ_{2100} = 5,400; I.R. bands at 1735 (acetate) and 1710 cm.$^{-1}$ (six-ring ketone). Found: C, 79.2; H, 11.1. $C_{32}H_{52}O_3$ requires C, 79.3; H, 10.8], which with mineral acid gives 7-oxo*iso*euph-13(17)-enyl acetate (III) [m.p. 112–113°, $[\alpha]_D$ −50° (*c*, 1.3), ϵ_{2100} = 6,700. Found: C, 79.6; H, 11.0. $C_{32}H_{52}O_3$ requires C, 79.3; H, 10.8]. Wolff-Kishner reduction of III, and reacetylation, gives *iso*euph-13(17)-enyl acetate (V)[5] [m.p. and mixture m.p. 110°, $[\alpha]_D$ −9° (*c*, 2.0). Found: C, 81.7; H, 11.7. Calc'd for $C_{32}H_{54}O_2$: C, 81.6; H, 11.6]. Oxidation of III with selenium dioxide yields 7-oxo*iso*eupha-11:13(17)-dienyl acetate [m.p. 107–109°, $[\alpha]_D$ −45° (*c*, 0.2), $\lambda_{max.}$ 2470, 2550 (log. ϵ = 4.33) and 2640 Å. Found: C, 79.4; H, 10.45. $C_{32}H_{50}O_3$ requires C, 79.6; H, 10.4]. Wolff-Kishner reduction of 7-oxo*apo*euph-14-enyl acetate (II), and re-acetylation gives *apo*euph-14-enyl acetate (IV) [m.p. 114–115°, $[\alpha]_D$ −12° (*c*, 1.1), ϵ_{2100} = 5,300. Found: C, 81.5; H, 11.7. $C_{32}H_{54}O_2$ requires C, 81.6; H, 11.6] isomerized by a short treatment with dry hydrogen chloride at 0° to *iso*euph-13(17)-enyl acetate (V)[5] [m.p. and mixture m.p. 109–110°, $[\alpha]_D$ −10° (*c*, 0.4)]. These acid conditions have no effect upon euph-8-enyl acetate and simply convert dihydrobutyrospermyl acetate (I, R = Ac) into euph-8-enyl acetate.[1] Selenium dioxide converts 7-oxo*apo*euph-14-enyl acetate (II) into 7-oxo*apo*eupha-5:14-dienyl acetate [m.p. 103–104°, $[\alpha]_D$ −126° (*c*, 1.2), $\lambda_{max.}$ 2350 Å. (ϵ = 14,000). Found: C, 79.4; H, 10.4. $C_{32}H_{50}O_3$ requires C, 79.6; H, 10.4].



The oxidation of dihydrobutyrospermyl acetate to 7-oxo*apo*euph-14-enyl acetate (II) establishes that the double bond in the former is between C_7 and C_8. We understand that Professor E. R. H.

(1) D. S. Irvine, W. Lawrie, A. S. McNab, and F. S. Spring, *Chemistry & Industry*, 626 (1955).

(2) Specific rotations are for chloroform solutions at 15°.

(3) K. Seitz and O. Jeger, *Helv. Chim. Acta*, **32**, 1626 (1949); T. G. Halsall, *Chem. and Ind.*, 867 (1951).

(4) M. C. Dawson, T. G. Halsall, E. R. H. Jones, G. D. Meakins, and P. C. Phillips, *Chemistry & Industry*, 918 (1955); E. R. H. Jones and T. G. Halsall, *Fortschritte der Chemie organischer Naturstoffe*, Springer-Verlag, **XII**, 108 (1955).

(5) D. H. R. Barton, J. F. McGhie, M. K. Pradhan, and S. A. Knight, *J. Chem. Soc.*, 876 (1955).

	M_D						
	Alcohol	Acetate	Benzoate	Ketone	Δ_1	Δ_2	Δ_3
Lanost-7-enol (VI)	+45°	+156°	+267°	−85°	+111°	+222°	−130°
Dihydrobutyrospermol (I, R = H)	−60	+56	+164	−182	+116	+224	−122

Jones, F.R.S., and his collaborators, have reached the same conclusion using a different method. Of more importance, the reactions described above also show that the 9-hydrogen in butyrospermol is α-orientated. The methyl group migration included in the conversion of dihydrobutyrospermyl acetate into II is considered to synchronize with attack by the oxidizing agent at the double bond; accordingly the reaction does not involve the 9-hydrogen in dihydrobutyrospermyl acetate which has the same orientation (α) as that in *iso*euph-13(17)-enyl acetate (V).

Although the change in molecular rotation on oxidation of many 3β-hydroxy-5α-steroids and 3β-hydroxytriterpenoids to the corresponding 3-ketones is positive, the change when butyrospermol and dihydrobutyrospermol (I, R = H) are oxidized to the corresponding 3-ketones is in each case negative.[6] As shown below, substitution of hydrogens at 4, 4′, and 14 in cholestanol and ergostanol by methyl groups has a considerable effect upon the contribution of ring A to the molecular rotation. Furthermore, the change in molecular rotation when lanost-7-en-3β-ol (VI) is oxidized to lanost-7-en-3-one [m.p. 146–147°, $[\alpha]_D$ −20° (*c*, 2.8). Found: C, 84.7; H, 12.0. $C_{30}H_{50}O$ requires C, 84.4; H, 11.8] is *negative* and almost identical with the related value for dihydrobutyrospermol. The close correspondence in the Δ_1, Δ_2, and Δ_3 values for lanost-7-en-3β-ol and dihydrobutyrospermol confirms the steric formula (I, R = H) proposed for the latter compound.

	M_D				
	Hydrocarbon	3β-Alcohol	3-Ketone	Δ_3	Δ_{CO}
Cholestane	+91°	+93°	+159°	+66°	+68°
Ergostane	+66	+64	+140	+76	+74
Lanostane	+149	+150	+116	−34	−33
Laudane	+107	+93	+62	−31	−45

We now formulate the euph-7-enyl acetate obtained from 7-oxoeuph-8-enyl acetate, by Wolff-Kishner reduction and re-acetylation,[5] as 9β-euph-7-enyl acetate. The method of formation requires that its 9-hydrogen has the more stable configuration and this must be β; 9β-euph-7-enyl acetate can assume an all-chair (or half-chair) conformation whereas that of 9α-euph-7-enyl acetate (dihydrobutyrospermyl acetate) includes a boat (or half-boat). 9β-Euph-7-enyl acetate is unchanged by treatment with hydrogen chloride using conditions which convert dihydrobutyrospermyl acetate (boat or half-boat) into euph-8-enyl acetate (all-chair or half-chair).

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(6) Sir Ian Heilbron, E. R. H. Jones, and P. A. Robins, *J. Chem. Soc.*, 444 (1949).