398. *Triterpenoids. Part L.* The Constitution of Butyrospermol.*

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Butyrospermol, a tetracyclic triterpenoid alcohol from shea-nut fat, has been converted into euphol. This and other reactions show that butyrospermol is either 9ξ-eupha-7 : 24-dien-3β-ol (IV) or 8ξ-eupha-9(11) : 24-dien-3β-ol (V).

In 1934, Heilbron, Moffet, and Spring [1] isolated an alcohol, which they named basseol, of approximate molecular formula $C_{30}H_{50}O$, from shea-nut fat. Basseol acetate, obtained from the acetylated non-saponifiable matter after separation of a fraction rich in β-amyrin, had m. p. 141°, $[\alpha]_D$ +22·4°,† and when hydrolysed with alkali gave basseol, m. p. 109·5°, $[\alpha]_D$ −11·9°. The presence in basseol acetate of two double bonds and hence its tetracyclic nature followed from its behaviour with perbenzoic acid. Beynon, Heilbron, and Spring [2] later claimed that treatment of basseol acetate with bromine, sulphuric–acetic acid, formic acid, hydrogen bromide in ether, or hydrogen chloride in chloroform gave β-amyrin acetate in yields of 50, 20, 13, 40, and 90% respectively, and they also reported that ozonolysis of basseol acetate yielded formaldehyde. A subsequent examination by Heilbron, Jones, and Robins [3] showed that, although, by using the original method, an acetate was isolated the physical constants of which (m. p. 139—141°, $[\alpha]_D$ +23°) approximate to those of basseol acetate, this acetate is not homogeneous since on repeated crystallisation it gave an ester, m. p. 146·5—147·5°, $[\alpha]_D$ +11°, which was named butyrospermyl acetate and on hydrolysis gave butyrospermol, m. p. 111—113°, $[\alpha]_D$ −12°. Of more importance, it was shown that the chemical properties of butyrospermyl acetate were

* Part XLIX, *J.*, 1956, 1949.

† Specific rotations given in this paper are for chloroform solutions.

[1] Heilbron, Moffet, and Spring, *J.*, 1934, 1583.

[2] Beynon, Heilbron, and Spring, *J.*, 1937, 989.

[3] Heilbron, Jones, and Robins, *J.*, 1949, 444.

different from those reported by Beynon, Heilbron, and Spring for basseol acetate; in particular, β-amyrin acetate was not isolated from any reaction product from pure butyrospermyl acetate and ozonolysis of the last compound gave acetone and not formaldehyde.

We have again examined the non-saponifiable matter from shea-nut fat and, using the original method, we had no difficulty in isolating an acetate whose constants (m. p. *ca.* 140°, $[\alpha]_D$ *ca.* +22°) are in good agreement with those reported for basseol acetate. We confirmed the heterogeneity of this acetate by many crystallisations from relatively dilute solutions and thereby obtained butyrospermyl acetate, m. p. 145°, $[\alpha]_D$ +11°; we also confirmed the observation that crude butyrospermyl acetate, $[\alpha]_D$ +22°, is not readily purified by crystallisation from more concentrated solutions. Dawson, Halsall, Jones, and Robins [4] have considered the possibility that basseol acetate was butyrospermyl acetate contaminated with *ca.* 16% of β-amyrin acetate and we believe this to be true. Alkaline hydrolysis of crude butyrospermyl acetate, $[\alpha]_D$ +22° (basseol acetate), and crystallisation of the product gave pure butyrospermol, m. p. 109—110°, $[\alpha]_D$ −12·5°, identical with a specimen prepared by hydrolysis of pure butyrospermyl acetate. The physical constants of butyrospermol are in excellent agreement with those of basseol, which in contrast to basseol acetate, was, we believe, a pure compound. Over a number of years, many different samples of shea-nut fat have been examined in this laboratory and with each sample the experience of Heilbron, Moffet, and Spring has been confirmed.

Some of the reactions of basseol acetate described by Beynon, Heilbron, and Spring are compatible with the view that it was butyrospermyl acetate contaminated with *ca.* 16% of β-amyrin acetate. On the other hand, the formation of β-amyrin acetate from basseol acetate in yields of 40, 50, and 90% reported above cannot be reconciled with this view and we suggest that the acetate used for the three experiments was not identical with the basseol acetate of Heilbron, Moffet, and Spring and was probably impure β-amyrin acetate.

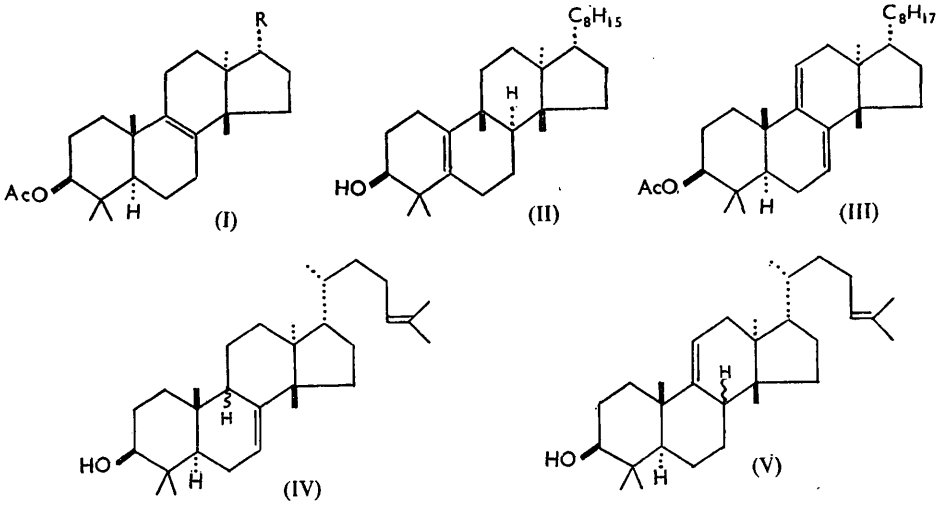
Previous studies [3,4] on butyrospermol have shown that it is a secondary alcohol, $C_{30}H_{50}O$ (or a near homologue), contains two double bonds, and is consequently tetracyclic. One of the double bonds is present as an *iso*propylidene group and is readily reduced. The second (less reactive) double bond is not reduced by platinum and hydrogen. From a study of the infrared spectrum of butyrospermene Jeger and Seitz [5] concluded that the less reactive double bond of butyrospermol is tetrasubstituted, and a consideration of the ultraviolet absorption of dihydrobutyrospermol led Halsall [6] to the same conclusion with the further limitation that the double bond is endocyclic. The experiments described below show that this double bond is tri- and not tetra-substituted.

Dawson *et al.*[4] showed that treatment of dihydrobutyrospermyl acetate for a short period with dry hydrogen chloride at 0° gives dihydro*iso*butyrospermyl acetate, and a consideration of the reactions of this isomer led them to suggest that its double bond corresponds in environment to that in lanost-7-enyl acetate, *i.e.*, that it is trisubstituted. The experiments described below show that the double bond in dihydro*iso*butyrospermyl acetate is tetra- and not tri-substituted. We have again prepared dihydro*iso*butyrospermyl acetate and we find that it is identical with euph-8-enyl acetate [7] (I; R = C_8H_{17}). The identity was confirmed by oxidation of dihydro*iso*butyrospermyl acetate to 7 : 11-dioxoeuph-8-enyl acetate [8,9] and by isomerisation of dihydro*iso*butyrospermyl acetate with hydrochloric–acetic acid to *iso*euphenyl acetate.[9] Dawson *et al.*[4] reported that dihydro-*iso*butyrospermyl acetate is extremely inert towards perbenzoic acid; after 23 days the equivalent of only 0·15 g.-atom of oxygen per mole was absorbed. This behaviour is not consonant with the fact that dihydro*iso*butyrospermyl acetate is identical with euph-8-enyl

[4] Dawson, Halsall, Jones, and Robins, *J.*, 1953, 586.
[5] Jeger and Seitz, *Helv. Chim. Acta*, 1949, **32**, 1626.
[6] Halsall, *Chem. and Ind.*, 1951, 867.
[7] Barton, McGhie, Pradhan, and Knight, *ibid.*, 1954, 1325; *J.*, 1955, 876; Arigoni, Viterbo, Dünnenberger, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1954, **37**, 2306; Ménard, Wyler, Hiestand, Arigoni, Jeger, and Ruzicka, *ibid.*, 1955, **38**, 1517.
[8] McDonald, Warren, and Williams, *J.*, 1949, S155; Haines and Warren, *J.*, 1950, 1562; Vilkas, *Bull. Soc. chim. France*, 1950, 582; Christen, Dünnenberger, Roth, Heusser, and Jeger, *Helv. Chim. Acta*, 1952, **35**, 1756.
[9] Vilkas, Dupont, and Dulou, *Bull. Soc. chim. France*, 1949, 813.

acetate which reacts with perbenzoic acid to yield an oxide [9,10] and we believe the report to be in error since in our hands dihydro*iso*butyrospermyl acetate was easily oxidised by perbenzoic acid to euph-8-enyl acetate oxide. The relation between butyrospermol and euphol has been confirmed by conversion of the former into the latter. Addition of one mol. of bromine to butyrospermyl acetate in chloroform and treatment of the solution with dry hydrogen chloride, followed by debromination of the product with zinc, gave euphyl acetate (I; R = C_8H_{15}).

At this stage in the investigation we argued that if the less reactive double bond in butyrospermol is tetrasubstituted [5,6] the alcohol must be (II). Doubt arose whether the less reactive double bond in butyrospermol is tetrasubstituted when we found that dihydro-



butyrospermyl acetate is isomerised to euph-8-enyl acetate by shaking it with platinum and hydrogen in acetic acid, a rearrangement independently observed and reported by Jones and his collaborators in a recent preliminary communication.[11] A detailed examination of the infrared spectra of dihydrobutyrospermyl acetate and related compounds also led these authors to the view that the less reactive double bond in butyrospermol is tri- and not tetra-substituted as originally inferred.[4,5,6] The ease with which dihydrobutyrospermyl acetate rearranges to euph-8-enyl acetate and the conflicting interpretations of the infrared data, led us to seek a chemical proof of the extent of substitution of this double bond. Treatment of dihydrobutyrospermyl acetate with osmic acid and acetylation of the product at either 20° or 100° gives a saturated triol diacetate from which we conclude that the less reactive double bond is tri- and not tetra-substituted. The triol diacetate is very readily converted into eupha-7 : 9(11)-dienyl acetate (III) [10,12] by heating it with acetic anhydride and potassium acetate, by heating it in a vacuum at 100°, by sublimation in a vacuum, and by heating it with zinc in acetic acid, behaviour which proves that dihydrobutyrospermyl acetate is a simple double-bond isomer of euph-8-enyl acetate, in which the unsaturated centre is either between $C_{(7)}$ and $C_{(8)}$ or between $C_{(9)}$ and $C_{(11)}$. Accordingly, butyrospermol is identified as either 9ξ-eupha-7 : 24-dienyl-3β-ol (IV) or 8ξ-eupha-9(11) : 24-dien-3β-ol (V).

Since the appearance of a preliminary communication from us [13] summarising the more important aspects of the work described above, Jones and his collaborators [11,14] have reported that they have also concluded that butyrospermol is either (IV) or (V) and they express a tentative preference for the 9β-form of (IV).

[10] Barbour, Bennett, and Warren, *J.*, 1951, 2540.
[11] Dawson, Halsall, Jones, Meakins, and Phillips, *Chem. and Ind.*, 1955, 918.
[12] Dawson, Halsall, and Swayne, *J.*, 1953, 590.
[13] Irvine, Lawrie, McNab, and Spring, *Chem. and Ind.*, 1955, 626.
[14] Halsall and Jones, *Fortschr. Chem. org. Naturstoffe*, 1955, **12**, 108.

Experimental

Specific rotations were measured in $CHCl_3$ solution and ultraviolet absorption spectra in EtOH solution. Light petroleum (b. p. 60—80°) and grade II alumina were used for chromatography.

Butyrospermol.—By using the method of Heilbron, Moffet, and Spring,[1] an acetate fraction (*ca.* 5 g.), m. p. 138—139°, $[\alpha]_D$ +22° (*c* 2·1), was obtained from the non-saponifiable matter (160 g.) from shea-nut. Repeated crystallisation of this fraction from concentrated solution in alcohol did not markedly change the m. p. (*ca.* 140°) or specific rotation ($[\alpha]_D$ *ca.* +22°). Nine recrystallisations of this mixture from dilute solutions in ethanol–ethyl acetate (10 : 3) [3] gave butyrospermyl acetate (1·4 g.) as needles, m. p. 145°, $[\alpha]_D$ +11° (*c* 2·0). Alkaline hydrolysis of butyrospermyl acetate gave butyrospermol as needles (from aqueous methanol), m. p. 109—110°, $[\alpha]_D$ −12·5° (*c* 1·1). Alkaline hydrolysis of crude butyrospermyl acetate (" basseol acetate," m. p. 140°, $[\alpha]_D$ +22°) (1 g.) and three crystallisations of the product from aqueous acetone gave butyrospermol (400 mg.), m. p. and mixed m. p. 109—110°, $[\alpha]_D$ −12·5° (*c* 1·1), acetylation of which yielded pure butyrospermyl acetate, m. p. 145°, $[\alpha]_D$ +11° (*c* 1·6).

Dihydroisobutyrospermyl Acetate (*Euph-8-enyl Acetate*).—Dihydrobutyrospermyl acetate [3] (m. p. 135—136·5°, $[\alpha]_D$ +10·7°) was treated with dry hydrogen chloride at 0° as described by Dawson *et al.*,[4] to give dihydro*iso*butyrospermyl acetate (needles from chloroform–methanol), m. p. 124·5—125·5°, $[\alpha]_D$ +33·6° (*c* 2·3), undepressed in m. p. when mixed with euph-8-enyl acetate,[15] m. p. 123·5—124°, $[\alpha]_D$ +34·5°. A solution of dihydro*iso*butyrospermyl acetate (82 mg.) in acetic acid (3 c.c.) containing concentrated hydrochloric acid (0·15 c.c.) was kept at 100° for 3 hr. The product, crystallised from chloroform–methanol, gave *iso*euphenyl acetate [9] (58 mg.) as plates, m. p. and mixed m. p. 111°, $[\alpha]_D$ −10° (*c* 1·6).

Oxidation of dihydro*iso*butyrospermyl acetate (137 mg.) with chromic acid in acetic acid, by the method described by McDonald *et al.*,[8] followed by chromatography of the product on alumina and crystallisation from methanol, gave 7 : 11-dioxoeuph-8-enyl acetate (40 mg.) as yellow needles, m. p. and mixed m. p. 110—111°, $[\alpha]_D$ +19·7° (*c* 1·0), $\lambda_{max.}$ 2710 Å (ε 8100).

Oxidation of Dihydroisobutyrospermyl Acetate with Perbenzoic Acid.—A solution of the dihydro-*iso*-acetate (100 mg.) in chloroform (4 c.c.) containing perbenzoic acid (472 mg.) was kept at 0° for 2 days and at room temperature for 2 days. The product was isolated in the usual way and crystallised from methanol, to give 8ξ : 9ξ-epoxyeuphanyl acetate [9,10] (64 mg.) as needles, m. p. and mixed m. p. 175—177°, $[\alpha]_D$ +62° (*c* 0·9).

Conversion of Butyrospermyl Acetate into Euphyl Acetate.—Butyrospermyl acetate (200 mg.) in chloroform (25 c.c.) was treated at 0° with a 1% solution of bromine in chloroform (6·8 c.c.). Dry hydrogen chloride was passed through the solution for 1½ hr. at 0°. The mixture was washed with sodium hydrogen carbonate solution, and the chloroform evaporated under reduced pressure. A solution of the residue in acetic acid (27 c.c.) was refluxed with zinc dust (2 g.) for 2 hr. and the product isolated in the usual way, to yield euphyl acetate [15] (40 mg.) (needles from chloroform–methanol), m. p. and mixed m. p. 106·5—107·5°, $[\alpha]_D$ +40° (*c* 0·8).

Treatment of Dihydrobutyrospermyl Acetate with Osmium Tetroxide.—Osmium tetroxide (1·62 g.) in ether (20 c.c.) was added to dihydrobutyrospermyl acetate (2·0 g.) in pyridine (20 c.c.), and the mixture kept in the dark for 12 days at 14°. After dilution with ether (100 c.c.), the mixture was refluxed for 1 hr. with lithium aluminium hydride (4·5 g.). The product was isolated in the usual manner and treated with acetic anhydride and pyridine mixture for 2 hr. at 100°. A solution of the dry acetylated product in light petroleum (150 c.c.) was chromatographed on alumina (60 g.). Light petroleum eluted dihydrobutyrospermyl acetate (800 mg.), m. p. and mixed m. p. 134—135°, $[\alpha]_D$ +10° (*c* 1·4). Light petroleum–benzene mixtures eluted fractions (1·12 g.), crystallisation of which gave the *triol diacetate* as prismatic needles, m. p. 181—182°, $[\alpha]_D$ −82° (*c* 1·2) (Found : C, 74·9; H, 10·9. $C_{34}H_{58}O_5$ requires C, 74·7; H, 10·7%). It does not give a colour with tetranitromethane in chloroform and is transparent to ultraviolet light. Hydrolysis of the triol diacetate with lithium aluminium hydride gives the triol as a colourless oil, acetylation of which (either at 20° or at 100°) regenerated the triol diacetate.

Eupha-7 : 9(11)-dienyl Acetate (III) *from the Triol Diacetate.*—(*a*) A mixture of the triol diacetate (200 mg.), acetic anhydride (25 c.c.), and freshly fused potassium acetate (300 mg.) was refluxed for 4 hr. The product was isolated by means of ether, and its solution in light petroleum

[15] Newbold and Spring, *J.*, 1944, 249.

(50 c.c.) chromatographed on alumina (6 g.). Light petroleum eluted a fraction which crystallised from methanol, to give eupha-7 : 9(11)-dienyl acetate (60 mg.) as needles, m. p. and mixed m. p. 111—112°, $[\alpha]_D$ −78° (*c* 1·0), $\lambda_{max.}$ 2320, 2400, and 2470 Å (ε 15,000, 17,000, and 10,500).

(*b*) The triol diacetate (125 mg.) was kept at 100° in a vacuum for 2 days. The solid [m. p. 120—155°, $\lambda_{max.}$ 2320, 2400, and 2470 Å (ε 5600, 6500, and 4200)] in light petroleum (25 c.c.) was chromatographed on alumina (4 g.). The fraction (40 mg.) eluted with light petroleum crystallised from methanol, to give the 7 : 9(11)-dienyl acetate as needles, m. p. and mixed m. p. 111—112°. Light petroleum–benzene mixtures eluted fractions crystallisation of which from chloroform–methanol gave the triol diacetate (60 mg.) as needles, m. p. 177—178° (no depression).

(*c*) The triol diacetate (100 mg.) was sublimed at 160—180°/0·4 mm. A solution of the sublimate (m. p. 70—90°) in light petroleum (25 c.c.) was chromatographed on alumina (3 g.). Elution with light petroleum gave the 7 : 9(11)-dienyl acetate (47 mg.), m. p. and mixed m. p. 111—112°. Benzene eluted a fraction, crystallisation of which gave the triol diacetate (30 mg.), m. p. 177—178° (no depression).

(*d*) A solution of the triol diacetate (100 mg.) in acetic acid (10 c.c.) was kept at 100° with zinc dust (600 mg.) for 2 hr. The product was isolated in the usual way and crystallised from methanol, to give the 7 : 9(11)-dienyl acetate (80 mg.), identified by m. p., mixed m. p., specific rotation, and ultraviolet absorption.

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