119. *The Chemistry of the Triterpenes. Part XVI.* The Action of Hydrogen Chloride on Butyrospermol.*

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Hydrogen chloride in chloroform adds on to the *iso*propylidene group of butyrospermol and simultaneously causes the isomerisation of the unreactive double bond, probably to a position corresponding to that occupied by the double bond of *iso*lanostenyl acetate. Dehydrochlorination of the " hydrochloride " gives a butyrospermol isomer containing a vinylidene group ($>C{:}CH_2$).

Recently the isolation of a new tetracyclic diethenoid triterpene-like alcohol, butyrospermol, was described by Heilbron, Jones, and Robins (*J.*, 1949, 444) and also by Seitz and Jeger (*Helv. Chim. Acta*, 1949, **32**, 1626). Butyrospermol contains an *iso*propylidene grouping and an unreactive double bond, and appears to be closely related to the tetracyclic triterpenes. Basseol, a similar tetracyclic diethenoid alcohol, from shea-nut fat (Heilbron, Moffet, and Spring, *J.*, 1934, 1583), isomerises with acid to β-amyrin (Beynon, Heilbron, and Spring, *J.*, 1937, 989). The action of acidic reagents on butyrospermol was therefore of considerable interest. However, in none of our experiments has any pentacyclic compound been obtained.

When butyrospermyl acetate was treated with hydrogen chloride in chloroform an addition compound was formed (cf. Heilbron, Jones, and Robins, *loc. cit.*) and since it could not be hydrogenated it appeared probable that the *iso*propylidene double bond had reacted with the hydrogen chloride. With boiling diethylaniline there was obtained an isomer of butyrospermyl acetate, *iso*butyrospermyl acetate, from which the corresponding alcohol and hence the benzoate were prepared. Treatment of the new acetate with hydrogen chloride in chloroform regenerated the " hydrochloride."

The infra-red spectrum of *iso*butyrospermyl acetate [band at 883 cm.$^{-1}$ (ms)] indicated the presence of a vinylidene group. Treatment of the acetate with osmium tetroxide yielded a complex which, after decomposition, gave a triol, and this on fission with periodic acid gave formaldehyde in good yield. Ozonolysis of *iso*butyrospermyl acetate yielded dihydroketonor*iso*butyrospermyl acetate which on hydrolysis gave the corresponding alcohol, $C_{29}H_{48}O_2$. Attempted hydrogenation of *iso*butyrospermyl acetate by using a palladium catalyst was unsuccessful, in contrast to the ready hydrogenation of butyrospermyl acetate, but with a platinum catalyst one mol. of hydrogen was taken up. The product was not dihydrobutyrospermyl acetate, but an isomer, dihydro*iso*butyrospermyl acetate.

These results clearly indicate that both double bonds are involved in the hydrogen chloride reaction. No addition occurred when dihydrobutyrospermyl acetate was treated with hydrogen chloride, but dihydro*iso*butyrospermyl acetate resulted. It was also

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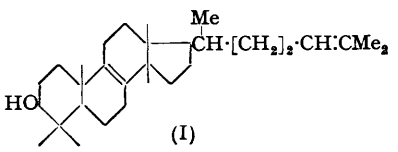
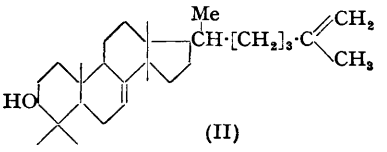
obtained when the " hydrochloride " was reduced with sodium and *iso*propanol. It can thus be concluded that in the hydrogen chloride reaction, addition takes place at the *iso*propylidene group, the unreactive double bond migrates, and on dehydrochlorination hydrogen is eliminated from one of the terminal methyl groups, *i.e.*, $>C{:}CMe_2 \longrightarrow >CH{\cdot}CClMe_2 \longrightarrow >CH{\cdot}CMe{:}CH_2$.

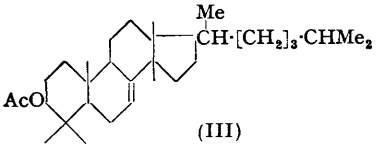
A compound analogous to the " hydrochloride " is formed under similar conditions by lanosteryl acetate, and on dehydrochlorination with alkali gives *iso*lanosterol (Dorée and Petrow, *J.*, 1936, 1562). In view of the formation of an *iso*propenyl group on dehydrochlorination of the " hydrochloride " from butyrospermyl acetate and of that from euphyl acetate (following paper), it is probable that *iso*lanosterol also contains an *iso*propenyl group and, based on the proposed structure (I) for lanosterol (Voser, Günthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1952, **35**, 66; Barnes, Barton, Cole, Fawcett, and Thomas, *Chem. and Ind.*, 1952, 426; Curtis, Fridricksons, and Mathieson, *Nature*, 1952, **170**, 321), is to be represented by (II). It is already known that the less reactive double bond of butyrospermol is tetrasubstituted (Seitz and Jeger, *loc. cit.*), and also that it is in a similar cyclic position to that in lanosterol (Halsall, *Chem. and Ind.*, 1951, 867). Cavalla, McGhie, and Pradhan (*J.*, 1951, 3142) and Barton, Fawcett, and Thomas (*J.*, 1951, 3147) have shown that in *iso*lanostenyl acetate (III), prepared by the action of hydrogen chloride on lanostenyl acetate, the double bond is trisubstituted and very unreactive. Hence if the carbon skeletons of butyrospermol and lanosterol are similar it is probable that the double bond in dihydro*iso*butyrospermol is trisubstituted as in *iso*lanostenol.



(I)



(II)



(III)

Perbenzoic acid titration of some of the above compounds under identical conditions revealed that with those subjected to hydrogen chloride treatment, the rate of absorption of oxygen by the less reactive ethylenic linkage was extremely slow and far from complete (Table 1).

TABLE 1.

Atoms oxygen absorbed after :	1	3	9	23 days
Butyrospermyl acetate	1·15	1·9	1·9	—
Dihydro*iso*butyrospermyl acetate	0·05	0·1	0·15	0·15
Dihydrobutyrospermyl acetate	0·95	1·0	1·05	—
Butyrospermyl acetate " hydrochloride "	0	0	0·05	0·2
*iso*Butyrospermyl acetate	0·95	1·05	1·10	1·05

The ultra-violet absorption of compounds of the dihydro*iso*-series has been determined in the 2000—2250 Å region (Table 2) and is consistent with the presence of a trisubstituted double bond (cf. Bladon, Henbest, and Woods, *J.*, 1952, 2737; Halsall, *loc. cit.*).

TABLE 2.

$\varepsilon_{obs.}$ in alcohol at :	2100 Å	2150 Å	2200 Å	2230 Å
Dihydrobutyrospermol	4200	3200	1900	1000
Dihydrobutyrospermyl acetate	4100	3100	1800	800
Dihydro*iso*butyrospermol	5100	3100	1550	—
Dihydro*iso*butyrospermyl acetate	4300	2700	1400	700

In view of both the extreme unreactivity of the double bond in dihydro*iso*butyrospermol towards per-acid, especially when compared with that of *iso*euphenyl acetate (cf. following

paper), and the ultra-violet absorption data, it is reasonable to conclude that the new double bond corresponds in environment to that in *iso*lanostenyl acetate.

When preparing butyrospermyl acetate from shea-nut fat great difficulty was experienced in eliminating β-amyrin acetate, and it was possible to obtain samples of seemingly nearly pure butyrospermyl acetate, m. p.s *ca.* 140—143° (*i.e.*, 3—4° low) [$(\alpha)_D$ *ca.* +20°), still containing 15—20% of β-amyrin acetate. We have failed repeatedly in attempts to obtain further samples of basseol, and recently Dr. G. D. Meakins has examined samples of fat from many different varieties of shea-nuts but in no case has any evidence of the presence of basseol been obtained. It must be considered whether the original basseol acetate was not in fact butyrospermyl acetate contaminated with β-amyrin acetate. The constants reported for basseol acetate (m. p. 141°; $[\alpha]_D$ +22·4°) agree well with those of our contaminated butyrospermyl acetate fractions, *i.e.*, a β-amyrin acetate content of *ca.* 16%. The presence of the β-amyrin acetate could explain the isolation of some of this compound in the isomerisation reactions, but the yields would be well below some of those described by the previous workers. Another possibility which needs further consideration is that the original fat emanated from a source other than shea-nuts.

A major difficulty in working with butyrospermol is the tedious isolation procedure. It forms only a few % of the non-saponifiable matter of shea-nut fat, and this in turn constitutes only 5—7% of the whole fat. It has now been found that, by allowing the fat to crystallise from an acetone solution at −80°, the non-saponifiable content remaining in solution is raised to about 60% (cf. Hilditch and Ichaporia, *J. Soc. Chem. Ind.*, 1938, **57**, 44).

Bauer and Moll (*Fette u. Seifen*, 1939, **46**, 530) reported the isolation of a new alcohol (parkeol), m. p. 164°, from shea-nut fat. In the present work an alcohol which is probably parkeol has been isolated. It has a similar m. p. (162—165°) and that of its acetate (154—157°) agrees with the m. p. of parkeyl acetate (154°).

Experimental

M. p.s were determined on a Kofler block and are corrected. Rotations were determined in chloroform. The alumina used for chromatography had an activity of I—II unless otherwise stated.

Preparation of the " Hydrochloride " from Butyrospermyl Acetate.—A solution of butyrospermyl acetate (500 mg.) in chloroform (15 c.c.) was cooled to 0° and a slow stream of dry hydrogen chloride was passed in for 2 hours. Evaporation under reduced pressure yielded a residue which was crystallised from ethanol to give the " *hydrochloride* " as needles, m. p. 139—141°, $[\alpha]_D^{19}$ +34° (*c*, 1·5) (Found : C, 76·0; H, 10·45. $C_{32}H_{53}O_2Cl$ requires C, 76·05; H, 10·55%). It gave a pale yellow colour with tetranitromethane.

iso*Butyrospermyl Acetate.*—The crude " hydrochloride " [obtained from butyrospermyl acetate (1 g.)] in diethylaniline (15 c.c.) was heated under reflux for 1 hour. The product was isolated with light petroleum (b. p. 40—60°) and yielded iso*butyrospermyl acetate* as needles (450 mg.) (from ethanol), m. p. 106—107·5°, $[\alpha]_D^{23}$ +34° (*c*, 1·6) (Found : C, 82·3; H, 11·15. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%). After 48 hours at 20° in sufficient ethanolic potassium hydroxide (10%) to effect solution, the acetate yielded iso*butyrospermol*, as fine needles [from light petroleum (b. p. 40—60°)], m. p. 60—67°, $[\alpha]_D^{16}$ +29° (*c*, 0·9) (Found : C, 83·9; H, 11·8. $C_{30}H_{50}O$ requires C, 84·45; H, 11·8%). The *benzoate*, prepared by benzoylation in pyridine, formed leaflets (from ethanol), m. p. 149—152°, $[\alpha]_D^{16}$ +60° (*c*, 0·8) (Found : C, 83·5; H, 10·25. $C_{37}H_{54}O_2$ requires C, 83·75; H, 10·25%).

*Dihydro*iso*butyrospermyl Acetate.*—(*a*) *iso*Butyrospermyl acetate (200 mg.) in methyl acetate (25 c.c.) was shaken with pre-reduced Adams's catalyst (20 mg.) and hydrogen at 20° until absorption of hydrogen ceased. After filtration and evaporation, elution of the residue with benzene–light petroleum (b. p. 60—80°) (1 : 19) from alumina (30 g.) yielded a fraction which was crystallised from ethanol, giving *dihydro*iso*butyrospermyl acetate* in good yield as needles, m. p. 125·5—127°, $[\alpha]_D^{18}$ +33° (*c*, 1·5) (Found : C, 82·0; H, 11·6. $C_{32}H_{54}O_2$ requires C, 81·65; H, 11·55%).

(*b*) Dihydrobutyrospermyl acetate (200 mg.) in chloroform (10 c.c.) was treated with hydrogen chloride as above. The product on crystallisation from aqueous ethanol gave dihydro-*iso*butyrospermyl acetate as needles (150 mg.), m. p. 124—127°, $[\alpha]_D^{18}$ +33°, identical with the product obtained by method (*a*).

(*c*) Butyrospermyl acetate " hydrochloride " (100 mg.) in *iso*propanol (25 c.c.) was treated with sodium (1·8 g.), and the mixture then heated at 100° for 1·5 hours. After the addition of ethanol (10 c.c.) the mixture was poured into excess of dilute acetic acid, and the product, isolated with ether, was acetylated at 20° in pyridine. Evaporation of the pyridine under reduced pressure and crystallisation of the residue from ethanol gave dihydro*iso*butyrospermyl acetate as needles (80 mg.), m. p. 124—127° undepressed on admixture with a sample obtained by method (*a*).

Action of Osmium Tetroxide on iso*Butyrospermyl Acetate*.—The acetate (1·0 g.) in dry ether (50 c.c.) was treated with osmic acid (550 mg.), and the solution kept at 20° for 7 days. The solution was evaporated to dryness under reduced pressure, and the residue refluxed for 4 hours with mannitol (3·2 g.) in ethanol (40 c.c.), benzene (40 c.c.), and potassium hydroxide (2 g.) dissolved in a little water. Dilution with dilute acetic acid and isolation with ether yielded a solid which was fractionated on deactivated alumina (activity III—IV; 25 g.). The fraction eluted with benzene–ether (4 : 1 and 1 : 1) gave the *triol*, crystallising from nitromethane as fine needles (250 mg.), m. p. 182—184°, $[\alpha]_D^{20}$ +19° (*c*, 1·3) (Found : C, 78·3; H, 11·3. $C_{30}H_{52}O_3$ requires C, 78·2; H, 11·4%).

Periodic Acid Fission of the Triol.—The triol (85 mg.) in methanol (6 c.c.) was treated with periodic acid (175 mg.) in water (3 c.c.), and set aside overnight at 20°. Water (10 c.c.) was then added and the whole distilled until 7·5 c.c. of distillate had been collected. Water (10 c.c.) was again added and a further 7·5 c.c. of distillate was collected. To each distillate was added a solution of 2 : 4-dinitrophenylhydrazine (1 g.) in sulphuric acid (4N; 45 c.c.). After an hour the distillates were extracted with benzene, and the extracts washed and dried. Chromatography of the extract of the first distillate gave no characterisable product. Chromatography of the extract of the second distillate gave formaldehyde 2 : 4-dinitrophenylhydrazone (35 mg.), m. p. 162—165° undepressed on admixture with an authentic specimen.

Ozonolysis of iso*Butyrospermyl Acetate*.—A solution of *iso*butyrospermyl acetate (1·2 g.) in ethyl acetate (50 c.c.) was cooled to −78°, and to it was added a saturated solution of ozone in ethyl acetate at −78° (35 c.c.) until a faint blue colour remained. The mixture was allowed to warm to 20° and the ethyl acetate was then evaporated under reduced pressure. The residue was taken up in benzene–light petroleum (1 : 9) and adsorbed on alumina (1200 g.). Elution with benzene gave a solid, crystallisation of which from ethyl acetate–methanol yielded *dihydroketonor*iso*butyrospermyl acetate* as needles (0·3 g.), m. p. 128—131°, $[\alpha]_D^{20}$ +31° (Found : C, 79·2; H, 10·7. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·7%). Hydrolysis of the acetoxy-norketone (54 mg.) in 1% methanolic potassium hydroxide (2 c.c.) for 96 hours at 20° gave *dihydroketonor*iso*butyrospermol* in good yield as needles from aqueous methanol, m. p. 169·5—173°, $[\alpha]_D^{20}$ +17° (Found : C, 81·1; H, 11·4. $C_{29}H_{48}O_2$ requires C, 81·25; H, 11·3%).

Isolation of Parkeol.—The non-saponifiable fraction (223 g.) of shea-nut fat was heated under reflux for 1½ hours with acetic anhydride. The mixture was kept at 20° for 18 hours, and the large mass of sticky solid which had formed was then filtered off. During the filtration more crystals (20 g.) separated from the filtrate. These were isolated and adsorbed from light petroleum (b. p. 60—80°) on alumina(1300 g.). After elution with light petroleum (b. p. 60—80°)–benzene (1 : 1), to remove butyrospermyl and β-amyrenyl acetates, elution with benzene gave a fraction (2·6 g.) which was crystallised several times from ethyl acetate–ethanol giving parkeyl acetate as needles, m. p. 154—157°, $[\alpha]_D^{20}$ +95° (Found : C, 82·05; H, 11·3. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). Hydrolysis of the acetate with 12% methanolic potassium hydroxide gave parkeol, needles (from alcohol), m. p. 162—165°, $[\alpha]_D^{20}$ +65°.

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