207. *The Characterisation of Basseol, a Tetracyclic Triterpene Alcohol, and its Isomerisation to β-Amyrenol.*

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The non-saponifiable matter of shea nut oil has been shown to contain illipene, β-amyrenol, lupeol, and a monohydric alcohol, m. p. 109·5° (Heilbron, Moffet, and Spring, J., 1934, 1583). With a view to locating a more prolific source of the last compound, for which the name basseol has been proposed (Beynon, Heilbron, and Spring, *Nature*, 1936, **138**, 1017), the non-saponifiable matters both of the cambium of the shea and of the bark of *Alstonia scholaris* have been examined. The fat from the latter does not contain basseol, the main components being the amyrenols, the β-isomer largely predominating, and lupeol (compare Ultée, *Chem. Weekblad*, 1914, **11**, 456).

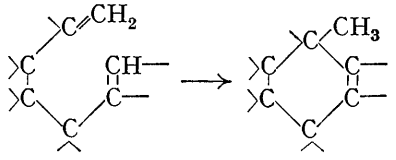
From the shea cambium, lupeol, α-amyrenol and basseol have been isolated, but since the yield of basseol does not compare favourably with that from the nut oil, the material used in the present investigation was obtained by the previously described method. Whereas shea nut oil contains β-amyrenol, only the α-isomer appears to be present in the cambium.

A preliminary examination of basseol (Heilbron, Moffet, and Spring, *loc. cit.*) showed that it is a diethenoid alcohol of the molecular formula $C_{30}H_{50}O$ or $C_{29}H_{48}O$. A decision in favour of the former has now been made, first, by the determination of the equivalent of basseol acetate and, secondly, by the isomerisation of this acetate to β-amyrenyl acetate by a variety of reagents such as bromine, the halogen acids, formic acid, and sulphuric acid. In view of this facile conversion of the diethenoid tetracyclic basseol into the monoethenoid pentacyclic β-amyrenol, a structural study of the former becomes of considerable importance in so far as the molecular configuration of the triterpene series as a whole is concerned.

A spectrographic examination of basseol acetate establishes that the two ethylenic linkages are not conjugated; catalytic hydrogenation shows that it absorbs only one mole

of hydrogen, giving *bassenyl acetate* (dihydrobasseol acetate), m. p. 119—120°, which is completely resistant to further hydrogenation, in this respect resembling β-amyrenyl acetate (Ruzicka, Huyser, Pfeiffer, and Seidel, *Annalen*, 1929, **471**, 21). Bassenyl acetate gives a yellow coloration with tetranitromethane in chloroform solution, absorbs one atom of oxygen on titration with perbenzoic acid, and, in contrast to basseol acetate, does not undergo ring closure.

The reactive ethylenic linkage of basseol has been diagnosed as an exocyclic methylene group, since basseol acetate, in contradistinction to bassenyl acetate, gives formaldehyde (20%) on ozonolysis; consequently the isomerisation of basseol to β-amyrenol may be represented by the scheme :—



From the non-volatile fraction of the products obtained by the ozonolysis of basseol acetate, β-amyrenyl acetate oxide (Spring, J., 1933, 1345) has been isolated; the oxidative degradation of both basseol and its dihydro-derivative is being further investigated.

Experimental.

The Non-saponifiable Matter of Shea Cambium.—The ground cambium (3 kg.) from large-girth trees was heated under reflux with successive portions of alcohol (6, 4, 4, 4 l.) for 3-hour periods. The combined extract was concentrated to approximately one quarter bulk and after the addition of a solution of potassium hydroxide (500 g.) in water (200 c.c.) was heated under reflux for 5 hours. After dilution with water, the solution was extracted with ether, and the extract washed successively with dilute hydrochloric acid and water. Removal of the solvent from the dried extract gave a light brown, resinous solid (50 g.), which showed no tendency to crystallise from a variety of solvents.

α-Amyrenyl Acetate.—The non-saponifiable matter (50 g.) was heated under reflux with acetic anhydride (150 c.c.) and anhydrous sodium acetate (25 g.) for 2½ hours and poured into alcohol (200 c.c.). The solid (A) separating overnight (m. p. 130—170°) was recrystallised from alcohol to give a crop (12 g.), m. p. 185—200°, repeated crystallisation of which from ethyl acetate yielded α-amyrenyl acetate (1·5 g.) in colourless plates, m. p. 222°, unchanged by further crystallisation or by admixture with an authentic specimen from *Manila elemi*; $[\alpha]_D^{20°}$ + 76° (l = 1, c = 5·0 in chloroform) (Found : C, 82·1; H, 11·0. Calc. for $C_{32}H_{52}O_2$: C, 81·95; H, 11·2%).

Basseol Acetate.—After concentration and standing, the filtrate from fraction A deposited a solid (10 g.), m. p. 85—95°, which after two crystallisations from ethyl acetate yielded rosettes of needles (2 g.), m. p. 141°, $[\alpha]_D^{18·5°}$ + 23° (l = 1, c = 1·95 in chloroform), unchanged by further crystallisation or by admixture with the acetate obtained by Heilbron, Moffet, and Spring (*loc. cit.*) from shea nut fat (Found : C, 81·9; H, 11·0. Calc. for $C_{32}H_{52}O_2$: C, 81·95; H, 11·2%).

Lupeol Benzoate and α-Amyrenyl Benzoate.—Concentration of the alcoholic mother-liquors from the fraction, m. p. 185—200°, gave successive crops which could not be further purified by crystallisation. These crops and their mother-liquors were combined, the solvent mixture removed under reduced pressure, the residual solid hydrolysed by heating under reflux with 7% alcoholic potassium hydroxide (500 c.c.) for 6 hours, and the solution largely diluted with water. The crystalline solid (10 g.) isolated by means of ether was benzoylated by heating under reflux for 5 hours with benzoyl chloride (20 c.c.), pyridine (15 c.c.), and dry benzene (100 c.c.). Removal of the solvent under reduced pressure yielded an oil, which was extracted with ether, the extract being washed successively with dilute sodium hydroxide solution, dilute sulphuric acid, and water. The solid obtained after removal of the solvent was repeatedly crystallised from benzene–alcohol; lupeol benzoate was then obtained in plates, $[\alpha]_D^{20°}$ + 60·3° (l = 1, c = 4·0 in chloroform), m. p. 265° either alone or in admixture with an authentic specimen (Found : C, 83·7; H, 10·1. Calc. for $C_{37}H_{54}O_2$: C, 83·7; H, 10·3%). Concentration of the mother-liquor from the first crystallisation of lupeol benzoate gave a solid, m. p. 85—95°, which on repeated crystallisation from benzene–alcohol yielded α-amyrenyl benzoate in hard needles, m. p. 194°, not depressed on admixture with an authentic specimen.

Molecular Weight of Basseol Acetate.—The acetate (400 mg.) was heated under reflux for 2 hours with alcoholic potassium hydroxide solution (40 c.c.; titre, 28·1 c.c. 0·1*N*-hydrochloric acid). The solution was diluted with alcohol (60 c.c.) and titrated with 0·1*N*-hydrochloric acid and phenolphthalein. The titre was standardised by comparison with that of a blank consisting of the same volume of alcoholic potassium hydroxide solution and alcohol. Basseol acetate: Found, *M*, 465, 464; $C_{32}H_{52}O_2$ requires *M*, 468. Cholesteryl acetate: Found, *M*, 431, 432; $C_{29}H_{48}O_2$ requires *M*, 428.

Isomerisation of Basseol Acetate.—(a) *Bromine.* A solution of bromine (0·68 g.; 2 mols.) in dry ether (50 c.c.) was added to basseol acetate (1 g.) in dry ether (100 c.c.), and the mixture set aside at room temperature for 8 hours and at − 5° for 10 hours. The oil obtained after removal of the solvent under reduced pressure was crystallised from ethyl acetate, from which β-amyrenyl acetate (0·5 g.) separated in needles, m. p. 236°, $[\alpha]_D^{19°}$ + 77° (*l* = 1, *c* = 0·05 in chloroform) (Found: C, 81·8; H, 11·4. Calc. for $C_{32}H_{52}O_2$: C, 81·95; H, 11·2%). The identity of the specimen was confirmed by hydrolysis and conversion of the crude amyrenol into the benzoate, which separated from benzene–alcohol in plates, m. p. 230° (Found: C, 83·6; H, 10·6. Calc. for $C_{37}H_{54}O_2$: C, 83·7; H, 10·3%). Furthermore, the melting points of the acetate and benzoate were unchanged on admixture with authentic specimens.

Solutions of basseol acetate (0·3 g.) in (b) a solution of sulphuric acid in acetic acid (2%, 30 c.c.), (c) formic acid (98%, 100 c.c.), (d) ethereal hydrogen bromide (3%, 150 c.c.), and (e) chloroform (75 c.c.) saturated at 0° with dry hydrogen chloride, were kept at 0° for 24 hours. In each case β-amyrenyl acetate (20, 13, 40, and 90% respectively) was isolated.

Bassenyl Acetate.—Basseol acetate (2 g.) in glacial acetic acid (140 c.c.) was shaken with hydrogen in the presence of Adams's catalyst (1 g.) at 75°, the hydrogen absorption (1 mol.) ceasing after 1 hour. The solution was diluted with water (200 c.c.), and the precipitated solid crystallised from aqueous alcohol, from which *bassenyl acetate* (1·8 g.) separated in needles, m. p. 119—120°, $[\alpha]_D^{20°}$ + 32·5° (*l* = 1, *c* = 0·8 in chloroform) (Found: C, 81·5; H, 11·5. $C_{32}H_{54}O_2$ requires C, 81·6; H, 11·6%). The acetate gives a pale yellow coloration with tetranitromethane in chloroform and a yellow colour with the Liebermann–Burchard reagent, the solution exhibiting a green fluorescence which is not so intense as that shown by basseol acetate. The acetate (0·37 g.) was set aside at 0° with a solution of perbenzoic acid in chloroform (100 c.c. of 0·2*N*). From time to time samples of the solution were titrated with 0·1*N*-sodium thiosulphate, all measurements being standardised against a blank consisting of the same volume of perbenzoic acid in chloroform. The following absorptions were observed:

Time (days)	1	2	3	4
Atoms of O absorbed per mole of acetate	0·76	0·89	1·01	1·01

Hydrolysis of bassenyl acetate gives bassenol as an oil. *Bassenyl benzoate* separates from alcohol in laminæ, m. p. 156°, $[\alpha]_D^{19°}$ + 48·1° (*l* = 1, *c* = 1·06 in chloroform) (Found: C, 83·6; H, 10·6. $C_{37}H_{56}O_2$ requires C, 83·4; H, 10·6%).

Ozonolysis of Basseol Acetate.—A slow stream of ozonised oxygen was passed through a suspension of basseol acetate (3·5 g.) in glacial acetic acid (60 c.c.) for 6 hours at room temperature, the issuing gases being bubbled through ice-cold water (100 c.c.). The solutions were mixed, diluted with water (200 c.c.), and distilled in steam until the distillate gave no turbidity with 2 : 4-dinitrophenylhydrazine hydrochloride solution. The distillate was nearly neutralised with sodium carbonate and again distilled in steam. The first fraction (100 c.c.) was boiled for 10 minutes with a solution of dimedon in water; the formaldehyde dimedon derivative (0·4 g., 20%) obtained separated from methyl alcohol in needles, m. p. 187°. The solid residue from the initial steam distillation was extracted with ether and washed with sodium hydroxide solution and water. Removal of the solvent gave a solid, which on crystallisation from methyl alcohol yielded β-amyrenyl acetate oxide in colourless laminæ, m. p. 288°, not depressed by admixture with the β-amyrenyl acetate oxide described by Spring (*loc. cit.*) and giving β-amyrenol oxide, m. p. 200—201°, on hydrolysis with 10% alcoholic potassium hydroxide (Found C, 79·5; H, 10·6. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%).

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