469. *Triterpenoids. Part LII.* The Constitution and Stereochemistry of Friedelin and Cerin.*

By GEORGE BROWNLIE, F. S. SPRING, ROBERT STEVENSON, and W. S. STRACHAN.

The constitution and stereochemistry of friedelin, a saturated ketone isolated from cork wax, have been determined. Dehydration of the related alcohol *epi*friedelanol gives an unsaturated hydrocarbon, friedel-3-ene, which is isomerised by mineral acid to a mixture of olean-13(18)-ene and 18α-olean-12-ene. This relation and other considerations lead to the formulation of friedelin as (X). Cerin is represented as 2β-hydroxyfriedelin (XXXII) and has been converted into friedelin.

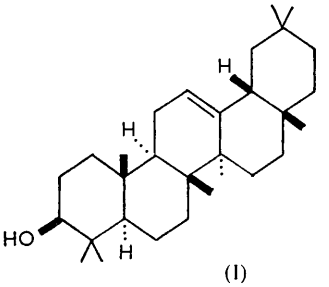
A DETAILED study of friedelin, isolated from cork wax, was first made by Drake and his collaborators [1–6] in whose papers references to earlier work will be found. They showed [1,2,3] that friedelin (friedelanone) is a saturated pentacyclic ketone, $C_{30}H_{50}O$, and that dehydrogenation of the alcohol friedelanol, obtained by reduction of friedelin with sodium and

* Part LI, preceding paper.

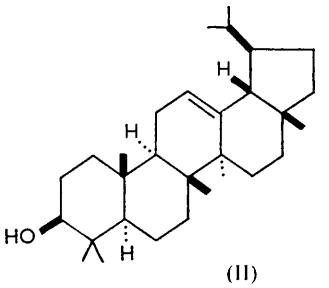
[1] Drake and Jacobsen, *J. Amer. Chem. Soc.*, 1935, **57**, 1570.
[2] Drake and Shrader, *ibid.*, p. 1854.
[3] Drake and Campbell, *ibid.*, 1936, **58**, 1681.
[4] Drake and Haskins, *ibid.*, p. 1684.
[5] Drake and Wolfe, *ibid.*, 1939, **61**, 3074.
[6] Drake and Wolfe, *ibid.*, 1940, **62**, 3018.

pentyl alcohol,[3] gives a mixture from which 1 : 8-dimethylpicene, 1 : 2 : 8-trimethylphenanthrene, 1 : 2 : 5 : 6-tetramethylnaphthalene, and 1 : 2 : 7- and 1 : 2 : 5-trimethylnaphthalene were isolated; [4,6] they concluded that friedelin is a perhydropolymethylpicene derivative.[6] A study by Ruzicka and Jeger and their collaborators [7,8] of some derivatives of friedelin showed that the carbonyl group is in a terminal ring and led them to the view that the cork ketone contains the fragment $\cdot CH_2 \cdot CH_2 \cdot CO \cdot CH \cdot CH \cdot$.

Our approach to a further elucidation of the structure of friedelin was direct. We assumed a biogenetic relation between friedelin and either β-amyrin (I) or α-amyrin (II), the parent alcohols of the oleanane and the ursane group of triterpenoids, members of



(I)



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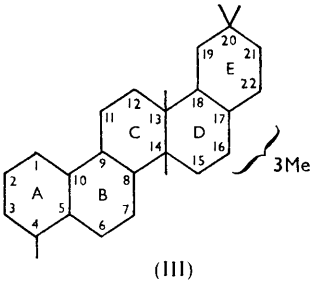

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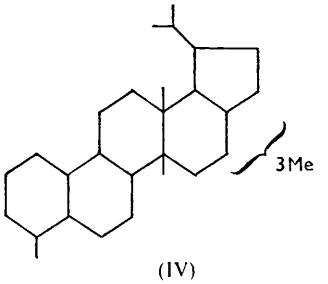


(IV)

each of which give 1 : 8-dimethylpicene on dehydrogenation. Starting from this postulate, we inferred from the conversion of friedelanol into 1 : 2 : 8-trimethylphenanthrene [4] that the carbocyclic structure of friedelane differs from that of oleanane and of ursane in having methyl groups attached to both $C_{(13)}$ and $C_{(14)}$ as in (III) and (IV). To test the initial postulate, we prepared the unsaturated hydrocarbon friedelene. Reduction of friedelin with lithium aluminium hydride gives *epi*friedelanol previously isolated from a lichen [9,10] and from *Ceratopetalum apetalum* D. Don;[10,11] *epi*friedelanol has also been obtained by catalytic reduction of friedelin [11] and it was probably prepared by Drake.[12] We find that *epi*friedelanol and friedelanol are both obtained by reduction of friedelin with sodium and pentyl alcohol for a short time. Dehydration of *epi*friedelanol by phosphorus oxychloride and pyridine gives the required hydrocarbon friedelene, the homogeneity of which was established by standard methods; a similar dehydration of *epi*friedelanol has been described [9] but the product was not characterised.

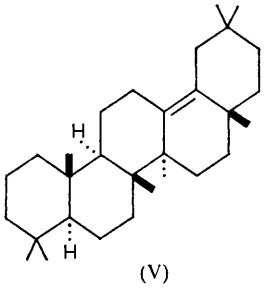
Hydrogenation of friedelene gives the saturated friedelane, which is identical with the hydrocarbon obtained from friedelin, by either the Wolff–Kishner or the Clemmensen method,[13] from which it follows that friedelene is formed from friedelin without a molecular rearrangement. The double bond in friedelene is trisubstituted since oxidation of the

[7] Ruzicka, Jeger, and Ringnes, *Helv. Chim. Acta*, 1944, **27**, 972.
[8] Perold, Meyerhans, Jeger, and Ruzicka, *ibid.*, 1949, **32**, 1246.
[9] Bruun, *Acta Chem. Scand.*, 1954, **8**, 71.
[10] Bruun and Jefferies, *ibid.*, p. 1948.
[11] Jefferies, *J.*, 1954, 473.
[12] Lander and Svirbely, *J. Amer. Chem. Soc.*, 1944, **66**, 235.
[13] Bruun, *Acta Chem. Scand.*, 1954, **8**, 76.

hydrocarbon with osmic acid gives a saturated glycol which forms a monoacetate only, and this is stable to chromic–acetic acid at room temperature.

Drake and Campbell [3] prepared a friedelene by thermal decomposition of friedelanyl benzoate. We have repeated this preparation many times and, using carefully purified friedelanyl benzoate, we obtain a hydrocarbon, the physical properties (melting point, mixed melting point, specific rotation, and infrared absorption) of which are almost indistinguishable from those of the hydrocarbon obtained by dehydration of *epi*friedelanol. The hydrocarbon obtained by pyrolysis of friedelanyl benzoate is a mixture, the major component of which is identical with the friedelene obtained from *epi*friedelanol, since oxidation of the pyrolysis hydrocarbon with osmic acid and acetylation of the product yields the diol monoacetate described above together with a smaller amount of a diol diacetate presumably formed by oxidation of another component of the mixture.

Treatment of friedelene, obtained from *epi*friedelanol, with hydrochloric–acetic acid gives a product, repeated crystallisation of which yields a mixed crystal of olean-13(18)-ene (V) and 18α-olean-12-ene. This mixed crystal is identical with that obtained by the same mineral acid treatment of olean-12-ene and recently described and identified by Brownlie *et al.*[14] The conversion of friedelene into olean-13(18)-ene, first described in a preliminary communication from this Laboratory,[15] shows that friedelane is (III) and not (IV) and it also discloses the principal features of the chemistry and stereochemistry of friedelin. The conversion of friedelene into olean-13(18)-ene by acid rearrangement proves that the carbonyl group in friedelin is in the terminal ring A and not in ring E, and that the cation (VI), or its equivalent, participates in the rearrangement. A number of rearrangements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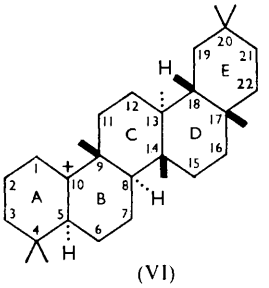
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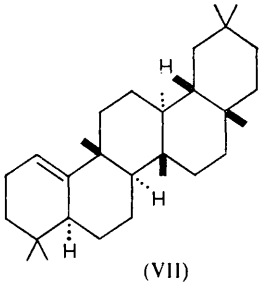
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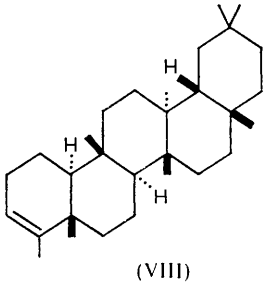
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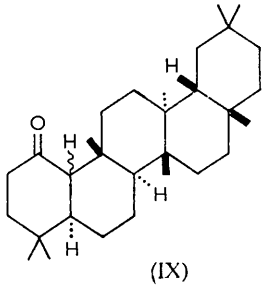
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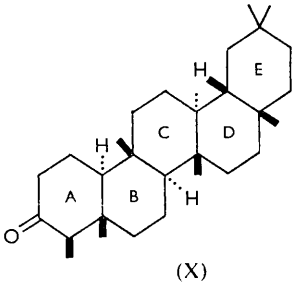

(X)

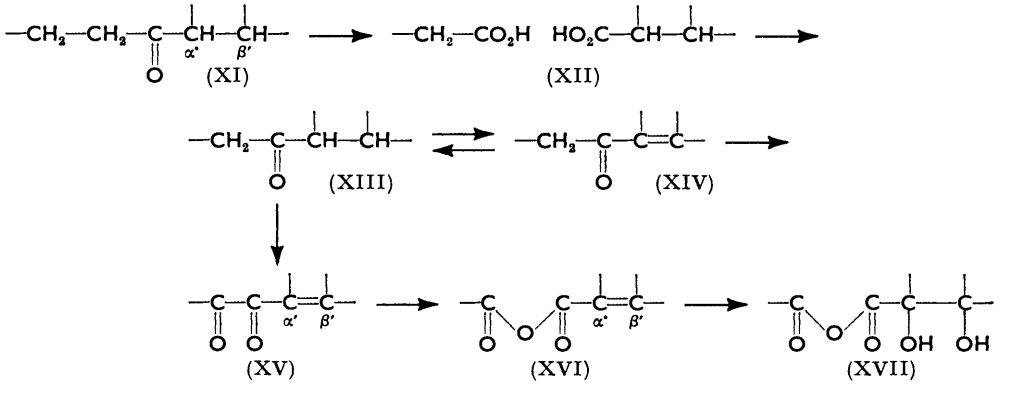
which closely resemble the friedelene ⟶ olean-13(18)-ene transformation have recently been examined and in each it has been established that a *cis*-locking of rings D/E is essential;[16] for this reason we ascribe the β-configuration to the 18-hydrogen atom in (VI). The subsequent behaviour of the cation (VI) follows the now familiar pattern of similar back-bone rearrangements,[16] the axial groups or atoms attached to $C_{(9)}$, $C_{(8)}$, $C_{(14)}$, and $C_{(13)}$ migrating

[14] Brownlie, Fayez, Spring, Stevenson, and Strachan, *J.*, 1956, 1377.
[15] Brownlie, Spring, Stevenson, and Strachan, *Chem. and Ind.*, 1955, 686.
[16] Allan, Spring, Stevenson, and Strachan, *J.*, 1955, 3371; Fayez, Grigor, Spring, and Stevenson, *J.*, 1955, 3378; Allan, Fayez, Spring, and Stevenson, *J.*, 1956, 465.

synchronously to $C_{(10)}$, $C_{(9)}$, $C_{(8)}$, and $C_{(14)}$ respectively, each migrating group retaining its axial configuration. Loss of a proton from either $C_{(12)}$ or $C_{(18)}$ gives olean-12- or -13(18)-ene, each of which is isomerised by mineral acid to the equilibrium mixture of olean-13(18)-ene (V) and 18α-olean-12-ene.[14]

The derivation of the structure and stereochemistry of the cationic intermediate (VI) shows that friedelene is either (VII) or (VIII). If friedelene is (VII), the cation (VI) is obtained by simple protonation of the double bond; and if the hydrocarbon is (VIII), the cation is developed by protonation of the double bond from the rear (α) side and synchronous movement of the axial 5-methyl group to $C_{(4)}$ and of the axial 10-hydrogen atom to $C_{(5)}$. The formulæ (VII) and (VIII) for friedelene correspond to the formulæ (IX) and (X) for friedelin. In our preliminary communication,[15] we concluded that (IX) represents friedelin because we then believed that (X) would not accommodate some of the reactions described and partly formulated by Ruzicka and Jeger.[7,8] However, contemporary studies on the ketone by Ourisson and Takahashi,[17] which were kindly communicated to us after the appearance of our preliminary note, showed that (IX) cannot represent friedelin. This emerged from their proof that friedonic acid, $C_{30}H_{50}O_3$, obtained by oxidation of friedelin with chromic acid,[3,5,7] is, in contrast to a previous report,[6] a methyl ketone. This important observation led us to reconsider (X) as the formula for friedelin, and this necessitated a revision of the partial formulæ proposed by Ruzicka and Jeger [7,8] for some of the derivatives of friedelin; a summarising account of the new considerations has been published.[18]

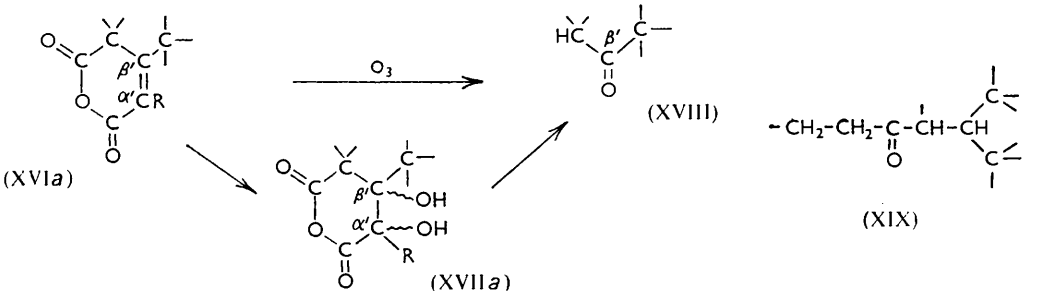
Oxidation of friedelin (XI) gives friedelindicarboxylic acid, $C_{30}H_{50}O_4$ (XII), the anhydride of which gives norfriedelanone, $C_{29}H_{48}O$ (XIII), on pyrolysis. Relatively mild oxidation of norfriedelanone with selenium dioxide gives an αβ-unsaturated ketone, norfriedelenone, $C_{29}H_{46}O$ (XIV), reduction of which regenerates the saturated norketone (XIII). Oxidation of norfriedelenone with selenium dioxide at 170—180° yields an un-



saturated α-diketone, norfriedelenedione, $C_{29}H_{44}O_2$ (XV), and this is also obtained by the same treatment of norfriedelanone (XIII). Hydrogen peroxide converts norfriedelenedione into an unsaturated dicarboxylic acid anhydride (XVI); comparison of the ultraviolet absorption spectra of the anhydride (XVI) and ketone (XV) confirms the relation implied by the partial formulæ. Oxidation of the unsaturated anhydride (XVI) with osmic acid gives a saturated glycol (XVII). Treatment of the glycol (XVII) with lead tetra-acetate or ozonisation of the unsaturated anhydride (XVI) gives a saturated tetracyclic ketone $C_{25}H_{42}O$. In the partial formulæ (XI)—(XV) used by Ruzicka, Jeger, and Ringnes,[7] the β′-carbon atom in (XI) is identified with the β′-carbon atom in (XV) and therefore with the β′-carbon atom in (XVI). In our view, the conversion of the unsaturated anhydride into the saturated tetracyclic ketone shows that the partial formula (XVI) for the former compound must be expanded to (XVI*a*) and that the formation of the saturated ketone

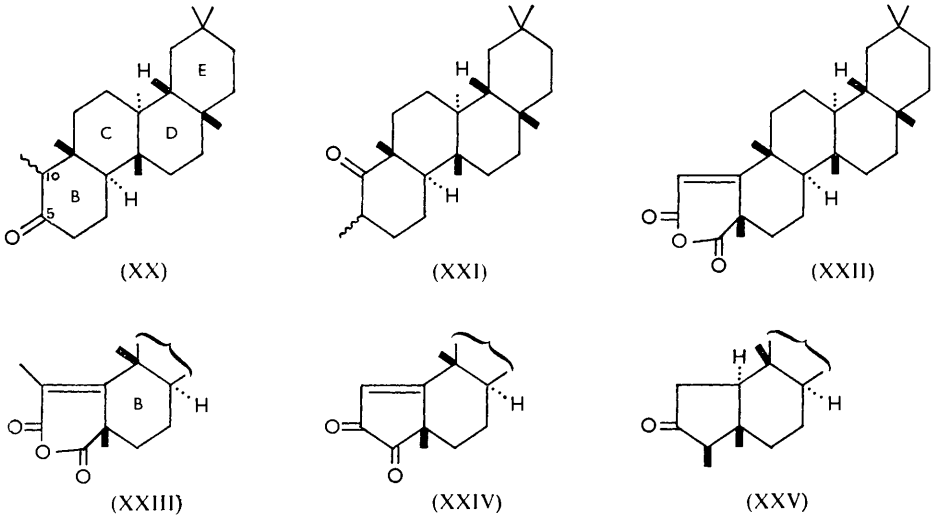
[17] Ourisson and Takahashi, *Chem. and Ind.*, 1955, 1155.
[18] Brownlie, Spring, Stevenson, and Strachan, *Chem. and Ind.*, 1955, 1156.

(XVIII) from (XVI*a*) and from the glycol (XVII*a*) is to be represented as illustrated. The carbonyl-carbon atom in the tetracyclic ketone (XVIII) is derived from the β′-carbon atom in friedelin (XI) and consequently this atom carries *only one* hydrogen atom. If



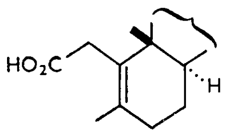
the partial formulæ for friedelin (XI) and for the enedione (XV) are correct relatively to each other, the former must be expanded to (XIX). Since this fragment is not present in (X), either the latter does not correctly represent the constitution of friedelin or the partial formulæ (XI) and (XV) do not correctly represent the relation between friedelin and the enedione. A decision in favour of the latter alternative was made as described below.

The methods by which the saturated tetracyclic ketone $C_{25}H_{42}O$ is obtained from friedelin establish that it is a substituted perhydrochrysene derived from rings B, C, D, and E of friedelin, and that its carbonyl group marks one of the A/B ring junctions in friedelin.



The exact molecular formula of the tetracyclic ketone ($C_{25}H_{42}O$) was established by Ruzicka and Jeger and their collaborators [8] by analysis of the tribromoacetate of the derived alcohol. Now, the structure and stereochemistry of rings B, C, D, and E in friedelin (apart from the nature of the substituent at $C_{(5)}$) follow from those of the cation (VI) and consequently only two formulæ, (XX) and (XXI), are to be considered for the tetracyclic ketone. Ourisson and Takahashi [17] have shown that the carbonyl group in the ketone $C_{25}H_{42}O$ has only one α-hydrogen atom. Together with the considerations discussed above, this important observation proves that the tetracyclic ketone is (XXI). The unsaturated dicarboxylic anhydride is consequently either (XXII) $C_{28}H_{42}O_3$ or (XXIII) $C_{29}H_{44}O_3$. Although most of the analytical data given by Ruzicka and Jeger and their collaborators [7,8] for the anhydride and its derivatives are in excellent agreement with either of these molecular

formulæ, the equivalent weight of the anhydride (Found : 214·1. $C_{29}H_{44}O_3$ requires 220·3. $C_{28}H_{42}O_3$ requires 213·3) and the elemental analysis of the derived glycol (XVII*a*) favour the molecular formula $C_{28}H_{42}O_3$. At a conservative evaluation, these data do not exclude the lower molecular formula (XXII) for the anhydride, and in our view this formula is more acceptable than (XXIII). To test the accuracy of the formula (XXII), Dr. Ourisson kindly undertook a determination of its molecular weight by the crystallographic method and this has unequivocally confirmed the formula $C_{28}H_{42}O_3$. We understand that this crystallographic examination will be described by Dr. Ourisson and Mlle. Sternberg. " Norfriedelenedione " is therefore identified as bisnorfriedelenedione (XXIV) and its formation from norfriedelanone (XXV) involves the extrusion of the 4-methyl group.



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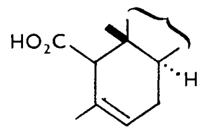
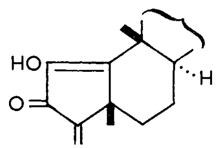


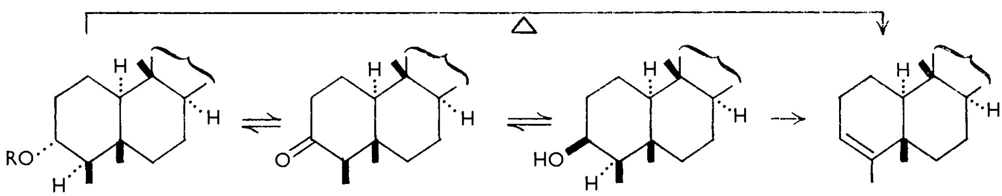
(XXVII)



(XXVIII)

Oxidation of bisnorfriedelenedione with alkaline hydrogen peroxide yields a βγ-unsaturated acid [8] which may be represented by either (XXVI) or (XXVII). Bromination of norfriedelenone and treatment of the product with alkali yields a norfriedelenedione which gives a colour with ferric chloride and forms an enol-acetate; we represent this norfriedelenedione as (XXVIII). The complex reactions of friedelin, including its conversion into olean-13(18)-ene, are thus adequately accommodated by the steric formula (X).

We next consider the configuration at $C_{(4)}$ in friedelin, the only centre of asymmetry not defined by the friedelene ⟶ olean-13(18)-ene rearrangement. Since friedelin is recovered unchanged after treatment with either alkali or acid the orientation of the 4-methyl group is the more stable of the two possible arrangements. Now friedelanol and *epi*friedelanol are $C_{(3)}$-epimers since each is reoxidised to friedelin (X) by chromic acid; friedelanol is the equatorial (α-)alcohol (XXIX; R = H) because it is formed from friedelin when equilibrating conditions are used and it is also formed when *epi*friedelanol is heated with



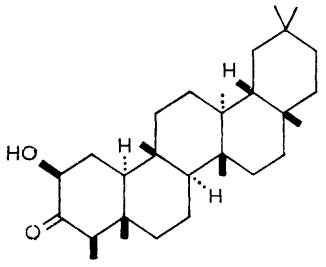
(XXIX) (X) (XXX) (XXXI)

sodium pentyloxide in air. The axial (β-)alcohol, *epi*friedelanol (XXX), is readily dehydrated under ionic conditions to give friedel-3-ene (XXXI) in high yield, from which we conclude that this 3 : 4-ionic elimination is *trans*-diaxial, *i.e.*, that the 4-methyl group is β-orientated. This decision is supported by the formation of friedel-3-ene (*cis*-elimination) by pyrolysis of friedelanyl benzoate (XXIX; R = Bz).

Friedelin contains an unhindered ketone group in that it reacts with the usual carbonyl reagents and is reduced to friedelane by the Clemmensen and Wolff–Kishner methods under normal (non-forcing) conditions. It is somewhat surprising, therefore, to find that reduction of friedelin with lithium aluminium hydride gives the axial alcohol *epi*friedelanol in high yield. We suggest that this is due to the directive effect of the 5β-axial methyl group which shields the carbonyl group from frontal attack. The terminal position of the carbonyl group, however, renders it fully exposed to attack from the rear; for this reason, we represent the product obtained by oxidation of friedel-3-ene (XXXI) with osmic acid as the

3α : 4α-diol. This behaviour of friedelin is comparable with that of cholestan-4-one [19] and in both cases it is to be attributed to the presence of an axial methyl group bearing a 1 : 3-relation to the carbonyl group. Another example of the directive effect exerted by the 5-axial methyl group is the hydrogenation of friedel-3-ene which gives friedelane in high yield.

The constitution of cerin, which occurs together with friedelin in cork wax, follows from that of friedelin (X). Cerin is a saturated α-hydroxy-ketone since on oxidation with chromic acid it gives a saturated α-diketone and friedelindicarboxylic acid $C_{30}H_{50}O_4$ (XII).[7] The infrared and the ultraviolet absorption spectrum of cerin show that the α-hydroxyl group is equatorial.[17] Cerin is therefore either 2β-hydroxyfriedelan-3-one (XXXII)



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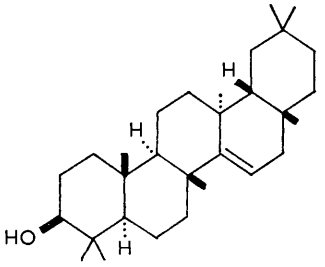

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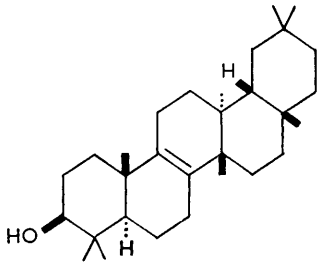

(XXXIV)

(2β-hydroxyfriedelin) or 3α-hydroxyfriedelan-2-one. We find that treatment of cerin acetate with zinc dust in acetic acid [20] gives friedelin from which we conclude that cerin is (XXXII).

The elucidation of the structure of friedelin and its conversion into olean-13(18)-ene support the initial postulate that β-amyrin (I) and friedelin (X) are genetically related. Taraxerol (XXXIII) [21] is considered to be an intermediate in the biogenetic degeneration of β-amyrin and we forecast that naturally occurring pentacyclic triterpenoids will be discovered, such as the euphol type (XXXIV), which will represent subsequent stages in the degeneration of taraxerol to friedelin.

A recent preliminary report of studies on friedelin by Corey and Ursprung [22] also describes the conversion of friedelin into olean-13(18)-ene. In agreement with Ourisson and Takahashi, the American authors conclude that the saturated tetracyclic ketone $C_{25}H_{42}O$ has only one replaceable α-hydrogen atom and they ascribe to this ketone the formula (XXI) deduced in the present paper and they also represent friedelin by (X). The latter formula has also been discussed in a recent paper by Dutler, Jeger, and Ruzicka.[23]

Experimental

Rotations were measured in $CHCl_3$ and ultraviolet absorption spectra in EtOH solutions. Grade II alumina and light petroleum, b. p. 60—80°, were used for chromatography.

Friedelin (*Friedelan-3-one*).—Cork (2 lb., 16—32 mesh) was extracted with boiling ethyl acetate (12 l.) for 4 hr. or with boiling benzene (12 l.) for 7 hr. The extracted matter was boiled with chloroform (800 c.c.), the mixture concentrated to 300 c.c., and, after cooling, the solid (4·3 g.) was collected. The filtrate was evaporated, and a solution of the residue in benzene was chromatographed on alumina (12″ × 1¼″). Elution with benzene (2 l.), followed by crystallisation of the eluate (3·5 g.) from chloroform–acetone, gave friedelin as needles, m. p. 255—262°, m. p. 264—266° (vac.), $[\alpha]_D$ −22°, −21° (*c* 2·3, 1·1). Drake and Jacobsen [1] give m. p. 255—261°, $[\alpha]_D$ −29°; Ruzicka, Jeger, and Ringnes [7] give m. p. 264—265° (vac.), $[\alpha]_D$ −28°; and Bruun [9]

[19] Jones, Lewis, Shoppee, and Summers, *J.*, 1955, 2876.
[20] Cf. Rosenfeld and Gallagher, *J. Amer. Chem. Soc.*, 1955, **77**, 4367.
[21] Beaton, Spring, Stevenson, and Stewart, *J.*, 1955, 2131.
[22] Corey and Ursprung, *J. Amer. Chem. Soc.*, 1955, **77**, 3667, 3668.
[23] Dutler, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1955, **38**, 1268.

gives m. p. 262—263° (vac.), $[\alpha]_D$ −21°. Friedelin was recovered unchanged after treatment with hydrochloric–acetic acid (3 : 10) at 100° for 24 hr.

Friedelan-3β-ol (epi*Friedelanol*) (XXX).—Lithium aluminium hydride (500 mg.) was added to a solution of friedelin (500 mg.) in ether (250 c.c.), and the mixture kept at 4° for 16 hr. The product was isolated in the usual way and crystallised from chloroform or chloroform–methanol, to give friedelan-3β-ol as blades, m. p. 279—283°, m. p. 287—288° (vac.), $[\alpha]_D$ +22° (*c* 0·3) (Found: C, 83·9; H, 12·2. Calc. for $C_{30}H_{52}O$: C, 84·0; H, 12·2%). Bruun and Jefferies [11] give m. p. 272—275°, 280—281° (vac.), $[\alpha]_D$ +20°.

Treatment of friedelan-3β-ol with acetic anhydride and pyridine at 100° for 1 hr. gave the acetate as plates (from chloroform–methanol), m. p. 288—290°, $[\alpha]_D$ +34° (*c* 0·75). Bruun and Jefferies [11] give m. p. 282—285°, $[\alpha]_D$ +35°. Hydrolysis of the acetate, by lithium aluminium hydride, gave friedelan-3β-ol, m. p. 287—289° (vac.), $[\alpha]_D$ +22° (*c* 0·3).

Friedelan-3β-ol (XXIX; R = H) (cf. Drake and Campbell [3]).—Sodium (3 g.) was added to a boiling solution of friedelin (1·19 g.) in *n*-pentyl alcohol (120 c.c.), and the mixture refluxed for 17 hr. The product was isolated in the usual way and its solution in benzene chromatographed on alumina. Elution with benzene (650 c.c.) yielded gummy solids (450 mg.). Elution with benzene–ether (1 : 1; 450 c.c.) gave fractions (610 mg.) which crystallised from chloroform–methanol to give friedelan-3β-ol as plates, m. p. 299—302°, $[\alpha]_D$ +18° (*c* 0·3). In another experiment in which the reflux time was 45 min., chromatography yielded, successively: friedelin, m. p. 255—258°, $[\alpha]_D$ −24° (*c* 1·5), eluted by benzene; friedelan-3β-ol, m. p. 277—280° (no depression), $[\alpha]_D$ +23° (*c* 0·6), eluted by benzene–ether (1 : 1); and friedelan-3α-ol, m. p. 300—305° (no depression), $[\alpha]_D$ +17° (*c* 0·3), eluted by ether. Drake and Campbell [3] give m. p. 301—304° for friedelanol.

Friedelan-3α-yl benzoate, prepared by treating the alcohol with pyridine and benzoyl chloride at 100° for 1 hr., crystallised from chloroform–methanol as needles, m. p. 248—249°, $[\alpha]_D$ −16°, −17° (*c* 1·4, 1·0). Drake and Campbell [3] give m. p. 250—251°.

Friedelan-3α-yl acetate, prepared in the usual way, crystallised from chloroform–methanol as plates, m. p. 316—318°, $[\alpha]_D$ −12° (*c* 1·0). Drake and Campbell [3] give m. p. 315—316°. Hydrolysis by lithium aluminium hydride gave friedelan-3α-ol as plates, m. p. 303—305°, $[\alpha]_D$ +18° (*c* 0·3).

Oxidation of friedelan-3α-ol with chromic acid in benzene–acetic acid at 30—40° gave friedelin as needles (from acetone–chloroform), m. p. 254—260° (no depression), $[\alpha]_D$ −20° (*c* 1·1).

Conversion of Friedelan-3β-ol into Friedelan-3α-ol.—A solution of *epi*friedelanol (200 mg.) in *n*-pentyl alcohol (30 c.c.) containing sodium *n*-pentyloxide (from 1 g. of sodium) was refluxed for 17 hr. The product (110 mg.; m. p. 295—300°) was crystallised from chloroform–methanol, to give friedelanol as plates, m. p. 298—300° (no depression).

Friedel-3-ene (XXXI).—Phosphorus oxychloride (15 c.c.) was added dropwise to a solution of friedelan-3β-ol (250 mg.) in pyridine (120 c.c.), and the mixture kept for 16 hr. at room temperature, then heated on the steam-bath for 30 min., cooled, and poured slowly on crushed ice. The product was isolated by extraction with light petroleum, and the dried extract filtered through alumina. Evaporation of the filtrate and crystallisation of the residue from chloroform–methanol gave *friedel-3-ene* as blades, m. p. 250—258°, m. p. 261—264° (vac.), $[\alpha]_D$ +53° (*c* 0·3), ε 4600 at 2040 Å (Found: C, 87·9; H, 12·5. $C_{30}H_{50}$ requires C, 87·7; H, 12·3%). It gives a pale yellow colour with tetranitromethane.

Pyrolysis of Friedelan-3α-yl Benzoate (cf. Drake and Campbell [3]).—The benzoate (250 mg.) was heated at 310° for 3 hr. in an atmosphere of nitrogen. A solution of the product in light petroleum was chromatographed on alumina. Light petroleum (30 c.c.) eluted a fraction (180 mg.) which crystallised from chloroform–methanol to give the hydrocarbon as blades, m. p. 256—258° (vac.), $[\alpha]_D$ +53° (*c* 0·5). A mixture with friedel-3-ene had m. p. 258—263° (vac.). Drake and Campbell [3] give m. p. 257—258° for a hydrocarbon prepared by this method.

Friedelane.—A solution of friedel-3-ene (150 mg.) in *cyclo*hexane (50 c.c.) and acetic acid (100 c.c.) was shaken with platinum (from 100 mg. of PtO_2) for 6 hr. at 60° in hydrogen. The product was crystallised from chloroform–methanol, to yield friedelane as plates, m. p. 248—250°, $[\alpha]_D$ +22° (*c* 0·9), which was undepressed in m. p. when mixed with a specimen, m. p. 248—250°, $[\alpha]_D$ +22° (*c* 0·6), prepared by Wolff–Kishner reduction of friedelin. Ruzicka, Jeger, and Ringnes [7] give m. p. 243—244°, $[\alpha]_D$ +42°; Huang-Minlon [24] gives m. p. 244—245°, $[\alpha]_D$ +42·5°; and Bruun [13] gives m. p. 245—246°, $[\alpha]_D$ +21°.

Friedelane-3α: 4α-diol.—Osmium tetroxide (370 mg.) in *cyclo*hexane (20 c.c.) was added to

[24] Huang-Minlon, *J. Amer. Chem. Soc.*, 1949, **71**, 3301.

a solution of friedel-3-ene (500 mg.) in *cyclo*hexane (200 c.c.) and the mixture set aside at room temperature for 14 days. Lithium aluminium hydride in ether was then added and the mixture kept overnight. Crystallisation of the product from methanol gave *friedelane*-3α : 4α-*diol* as plates, m. p. 243—245°, $[\alpha]_D$ +7° (*c* 0·8) (Found : C, 80·9; H, 11·7. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%). It does not give a colour with tetranitromethane in chloroform.

3α-*Acetoxyfriedelan*-4α-*ol*.—(*a*) Acetic anhydride (5 c.c.) was added to a solution of friedelane-3α : 4α-diol (250 mg.) in pyridine (10 c.c.) and the mixture heated at 100° for 2½ hr. or set aside overnight at room temperature. The product, isolated in the usual way and crystallised from chloroform–methanol, gave 3α-*acetoxyfriedelan*-4α-*ol* as needles, m. p. 252—254°, $[\alpha]_D$ +2°, +2° (*c* 2·0, 3·0) (Found : C, 78·9; H, 11·3. $C_{32}H_{54}O_3$ requires C, 79·0; H, 11·2%). It does not give a colour with tetranitromethane in chloroform. Infrared bands (in Nujol) at 1735, 1246, 1026, and 952 (acetate) and 3600 cm.$^{-1}$ (hydroxyl); we thank Dr. G. Eglinton for these data. Chromium trioxide (16·5 mg.) in acetic acid (21 c.c.) was added to 3α-acetoxyfriedelan-4α-ol (120 mg.) in acetic acid (50 c.c.). The mixture was kept overnight at room temperature, and worked up in the usual way, to give unchanged diol monoacetate as needles (114 mg.), m. p. and mixed m. p. 252—254°, $[\alpha]_D$ +2° (*c* 2·0). Hydrolysis of the diol monoacetate with 3% methanolic potassium hydroxide yielded the diol, m. p. and mixed m. p. 243—245°, $[\alpha]_D$ +7° (*c* 1·0).

(*b*) The hydrocarbon (500 mg.) obtained by pyrolysis of friedelanyl benzoate was treated with osmium tetroxide, as described above. A solution of the acetylated product in light petroleum was chromatographed on alumina. Elution with light petroleum–benzene (4 : 1) yielded 3α-acetoxyfriedelan-4α-ol (250 mg.) as plates, m. p. and mixed m. p. 252—254°. Elution with light petroleum–benzene (1 : 1) yielded a *diacetate* (80 mg.) as needles (from chloroform–methanol), m. p. 262—264°, $[\alpha]_D$ −40° (*c* 1·3) (Found : C, 77·0; H, 10·7. $C_{34}H_{56}O_4$ requires C, 77·2; H, 10·7%).

Conversion of Friedel-3-*ene into Olean*-13(18)-*ene and* 18α-*Olean*-12-*ene*.—A solution of friedel-3-ene (350 mg.) in acetic acid (450 c.c.) and concentrated hydrochloric acid (100 c.c.) was refluxed for 18 hr. A solution of the product in light petroleum was filtered through alumina; the eluate (290 mg.) crystallised from chloroform–methanol as blades, m. p. 184—185°, $[\alpha]_D$ −9·5° (*c* 0·8), which after four recrystallisations from the same solvent gave the mixed crystal of olean-13(18)-ene and 18α-olean-12-ene as blades, m. p. 186—187°, $[\alpha]_D$ −20° (*c* 1·0); further recrystallisation did not alter the m. p. or specific rotation. Mixtures with specimens obtained by mineral acid isomerisation of olean-12-ene, olean-13(18)-ene, 18α-olean-12-ene, and olean-18-ene [14] had the same m. p.

Friedelin from Cerin Acetate.—A solution of cerin acetate (176 mg.; m. p. 262—263°, $[\alpha]_D$ −36°) in acetic acid (100 c.c.) was refluxed with zinc dust (17·6 g.) for 24 hr. The product was isolated by extraction with ether–benzene, and its solution in light petroleum was chromatographed on alumina (4″ × ½″). After elution with light petroleum (200 c.c.) and light petroleum–benzene (4 : 1, 50 c.c.), further washing with this mixture (50 c.c.) eluted crystals (90 mg.), recrystallisation of which from chloroform–methanol yielded friedelin as needles (77 mg.), m. p. 255—260°, m. p. and mixed m. p. 262—265° (vac.), $[\alpha]_D$ −23° (*c* 2·15).

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