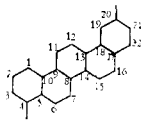
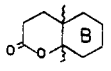
11.07; (2) addition of bromine to Δ^2-friedelene,[5] m.p. 257–258°, followed by dehydrobromination to give the exomethylenic diene III, m.p. 240–244°, $[\alpha]^{25}D$ +48.4°, λ_{max} 241 mμ (log ε 4.30), infrared max. 883 cm.$^{-1}$. Found: C, 87.84; H, 12.32.

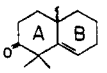


I



II

III

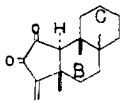


IV

Bromination of friedelin produces a 2-bromofriedelin, m.p. 210° (dec.), $[\alpha]^{25}D$ −140°, infrared, ultraviolet max. 1710 cm.$^{-1}$, 311 mμ (axial Br); found: C, 71.07; H, 9.65; Br, 15.38; location of bromine at C_2 proved by conversion to Δ^2-friedelene.[5] Bromination of friedelin enol benzoate furnishes 4-bromofriedelin, m.p. 196–197° (dec.), $[\alpha]^{25}D$ +90.5°, infrared, ultraviolet max. 1715 cm.$^{-1}$, 310 mμ (axial Br); Found: C, 70.44; H, 9.38; Br, 15.70. Although 2-bromofriedelin is unreactive toward silver acetate, 4-bromofriedelin is readily dehydrobrominated to an unsaturated, unconjugated ketone IV, which is not isomerized to a conjugated structure, m.p. 247–248°, $[\alpha]^{25}D$ −48.6°, infrared, ultraviolet max. 1710 cm.$^{-1}$, 290 mμ; Found: C, 84.87; H, 11.20. Wolff–Kishner reduction of IV produces a new olefin, m.p. 221–222°, different from Δ^2- and Δ^3-friedelenes.[5] The production of IV from 4-bromofriedelin indicates that migration of a methyl group at C_5 has occurred during dehydrobromination.

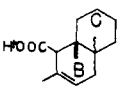
2-Bromofriedelin is not epimerized by hydrogen bromide, which proves the *trans*-locking of rings A and B and the presence of a hydrogen at C_{10}.[6] The change in molecular rotation due to axial bromine at C_2(ΔM_D −651°) is opposite in direction to that due to axial bromine at C_4(ΔM_D +614°). These data together with data on axial α-bromoketosteroids[7] reveal that (1) bromine is α-oriented in both 2- and 4-bromofriedelins and (2) the methyl at C_5 is β and the hydrogen at C_{10} is α.

Stepwise oxidation of norfriedelendione (V)[3] by hydrogen peroxide and ozone produces a tetracyclic saturated ketone, $C_{25}H_{42}O^8$ (VI), which possesses the oxo function at C_{10} (original numbering). Treatment of VI with excess deuterium bromide results in incorporation of only one deuterium atom/molecule proving the presence of a methyl group at C_9 and confirming the presence of a methyl group at C_5.

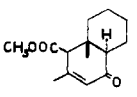


V

VI



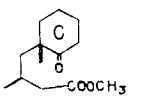
VII



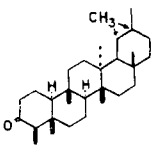
VIII

Oxidation of norfriedelendione with alkaline peroxide produces a β,γ-unsaturated acid,[8] $C_{26}H_{42}O_2$, VII. Sodium dichromate oxidation of the methyl ester of VII yields the unsaturated keto ester VIII, m.p. 150–151°, $[\alpha]^{25}D$ −42.7°, ultraviolet max. 247 mμ (log ε 3.97), infrared max. 1742; Found: C, 78.49; H, 10.05. Alcoholysis of VIII provides an unsaturated ketone (IX), m.p. 191–192°, $[\alpha]^{25}D$ −19.5°, ultraviolet max. 248 mμ (log ε 3.94), infrared max. 1664 cm.$^{-1}$; Found: C, 84.33; H, 11.38, which upon hydrogenation yields the corresponding saturated ketone X, m.p. 195–197°, $[\alpha]^{25}D$ +42.5°, infrared max. 1707 cm.$^{-1}$; Found: C, 84.02; H, 11.88.

X



XII



XIII

The presence of a hydrogen at the original C_8 is indicated by deuterium exchange of X with deuterium bromide (2.9 deuterium atoms/molecule) and by the three-step conversion of X via the keto acid XI to the keto methyl ester XII, m.p. 132–133°, $[\alpha]^{25}D$ +21.1°, infrared max. 1736, 1713, 1696 (weak) cm.$^{-1}$; Found: C, 77.38, H, 10.91.

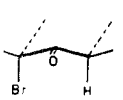
It is apparent that rings B and C and rings C and D in friedelin are *trans*-locked, both from chemical evidence[5] and from the molecular dimensions (1/4 unit cell) of friedelan-3α-ol chloroacetate, 16.5 × 6.5 × 6.9 Å. as determined by X-ray studies.[5,9]

The four remaining methyl groups of friedelin may be located as follows. Methyl groups must be present at C_{13} and at C_{14} since 1,2,7-trimethylnaphthalene and 1,2,8-trimethylphenanthrene are formed by selenium dehydrogenation of friedelan-3α-ol.[2] The presence of a third methyl group at C_{17} and the fourth at C_{19} or C_{20} is highly probable on biosynthetic grounds[10] because of the probable common genesis of friedelin and the other pentacyclic triterpenes from squalene. Thus, expanded structure XIII follows for friedelin.

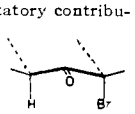
(5) To be described in full later.

(6) Otherwise the 2(axial)-bromoketone would be epimerizable, E. J. Corey, *ibid.*, **76**, 175 (1954).

(7) An axial bromine in the unit (a) makes a levorotatory contribution whereas that in the unit (b) makes a dextrorotatory contribution. For example, *e.g.* ΔM_D for 5α-bromo-6-ketocholestanyl acetate is −645° while that for 7α-bromo-6-ketocholestanyl acetate is +260°.



(a)



(b)

(8) G. W. Perold, K. Meyerhans, O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1246 (1949).

(9) *Cf.* methyl iodoacetyloleanolate 16.1 × 6.3 × 7.7 Å. [A. M. Abd El Rahim and C. H. Carlisle, *Chem. and Ind.*, 279 (1954)].

(10) L. Ruzicka, A. Eschenmoser and H. Heusser, *Experientia*, **9**, 357 (1953).

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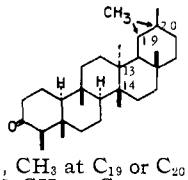
RECEIVED MAY 19, 1955

PROOF OF THE CONSTITUTION OF FRIEDELIN BY MULTI-GROUP REARRANGEMENT OF FRIEDELAN-3β-OL TO OLEAN-13(18)-ENE

Sir:

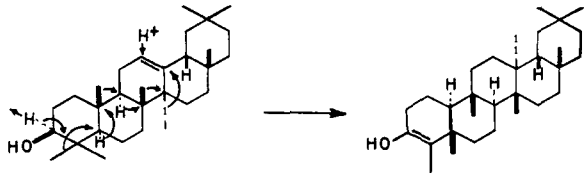
Formula I has been derived for friedelin by the studies described in the previous communication.[1] This structure bears a most interesting relationship to the three known classes of pentacyclic triterpenes and suggests a biosynthetic pathway starting from α- or β-amyrin which involves a series of consecutive 1,2-shifts of methyl groups and hydrogen

(1) E. J. Corey and J. J. Ursprung, THIS JOURNAL, **77**, 3667 (1955).



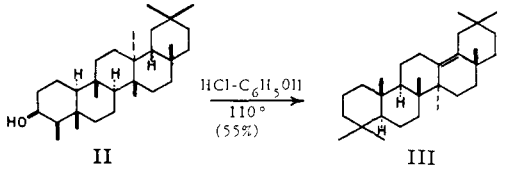
I, CH_3 at C_{19} or C_{20}
V, CH_3 at C_{20}

atoms away from ring A and toward ring E. Consideration of friedelin as a possible rearrangement product of α- or β-amyrin prompted us to undertake the experiments which are outlined in this report and which have led to the direct correlation of friedelin with β-amyrin.



β-amyrin friedelin(enol)

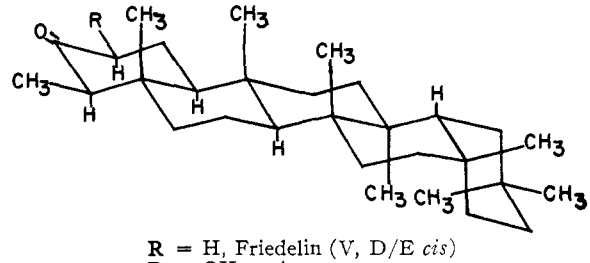
Reduction of friedelin with lithium aluminum hydride produces friedelan-3β-ol (II), m.p. 283.5–285°,[2,3] in which the hydroxyl function is axial. Treatment of II with hydrogen chloride in phenol at 110° causes a remarkable multi-group rearrangement which affords olean-13(18)-ene (III) (55% yield), m.p. 186–187°, $[\alpha]_D$ −12.5° (*C*, 0.80, chloroform), λ_{max} 213 mμ (log ϵ 3.51), bright yellow coloration with tetranitromethane, *Anal.* Calcd. for $C_{30}H_{50}$: C, 87.73, H, 12.27. Found: C, 87.76, H, 12.37. This material is identical with an authentic sample prepared from β-amyrin by oxidation, Wolff–Kishner reduction and acid-catalyzed isomerization of the 12,13-double bond to the 13,18-position, m.p. 186–187° (undepressed upon admixture with a sample from rearrangement of freidelan-3β-ol), $[\alpha]^{25}D$ −13.9° (*C*, 0.79, chloroform) bright yellow coloration with tetranitromethane. The infrared spectra of the above samples of $\Delta^{13(18)}$-olefin are identical.[4] Further confirmation of identity was obtained by conversion of both products to the same mixture of epimeric oxides with perbenzoic acid, m.p. *ca.* 191–5°, undepressed upon admixture. Both samples of oxide upon treatment with boron trifluoride ethereate yielded olean-11, 13(18)-diene (IV)[4], m.p. 219–220°, $[\alpha]^{25}D$ −72.4° (*C*, 0.95, chloroform), λ_{max} 242, 250, 260 mμ (log ϵ 4.44, 4.50, 4.31), *Anal.* Calcd. for $C_{30}H_{48}$: C, 88.16, H, 11.84. Found: C, 88.02; H, 11.91, brown coloration with tetranitromethane, mixture m.p. undepressed.



II III

The conversion of II into III proves the location of methyl groups at C_{17} and C_{20} as in β-amyrin and, together with the degradative work, establishes beyond any doubt structure V for friedelin, which is complete except for the orientation of the hydrogen at C_{18}.

The biosynthetic pathway for the conversion of lupeol (VI)[5] into friedelin by a sequence of 1,2-shifts would lead not only to the correct carbon skeleton, but also to the experimentally established stereochemical configuration at all asymmetric centers and to the β-orientation of the hydrogen at C_{18} (D/E *cis*) as in α[6]- and β-amyrin.[7] For this



R = H, Friedelin (V, D/E *cis*)
R = OH, cerin

reason we favor the view that the hydrogen at C_{18} in friedelin is β-oriented.[8]

If the above biosynthetic pathway is correct, two sequences for formation of pentacyclic triterpenes follow: (1) lupeol → β-amyrin → friedelin and (2) lupeol → α-amyrin → presently unknown relative of friedelin. We are currently engaged in a search for the missing α-amyrin analog of friedelin as well as for other intermediates in both series.

The formulation of cerin as 2β-hydroxy friedelin follows from the location of the hydroxyl at C_2 and from the fact that the hydroxyl is very easily acylated or sulfonated (equatorial orientation).

In connection with the work in this and the preceding paper, we wish to express our thanks to Dr. I. H. Riley for the X-ray measurements, to Dr. R. A. Sneen for the deuterium analyses, to Messrs. H. C. Huang, D. F. Joesting and R. G. Schultz for help in isolation of friedelin and preparation of intermediates, to the Armstrong Cork Company for supplies of cork wax and to the Eli Lilly Company for generous financial support.

(2) J. J. Lander and W. J. Svirbely, THIS JOURNAL, **66**, 235 (1944).

(3) Recently isolated from various natural sources by P. R. Jefferies, *J. Chem. Soc.*, 473 (1954), and by T. Bruun, *Acta Chem. Scand.*, **8**, 71 (1954).

(4) K. Takeda, *J. Pharm. Soc. Japan*, **63**, 197 (1943); *C. A.*, **45** 586 (1951).

(5) See L. Ruzicka, A. Eschenmoser and H. Heusser, *Experientia*, **9**, 357 (1953).

(6) E. J. Corey and J. J. Ursprung, *Chem. and Ind.*, 1387 (1954).

(7) D. H. R. Barton and N. J. Holness, *J. Chem. Soc.*, 78 (1952).

(8) This view is confirmed by a 2-dimensional Fourier X-ray analysis on friedelan-3α-ol chloro and bromoacetates made in these Laboratories by Dr. I. H. Riley, the results of which are completely concordant with structure V (D/E *cis*) for friedelin. These results will be reported later.

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RECEIVED MAY 19, 1955

LUMINESCENCE SPECTROSCOPY OF PORPHYRIN-LIKE MOLECULES INCLUDING THE CHLOROPHYLLS[1]

Sir:

The understanding of the participation of the chlorophylls in the primary reaction of photosynthesis demands an exact knowledge of the location and characteristics of the lowest excited states of these molecules.[2]

(1) Work done under a contract between the Office of Naval Research, U. S. Navy, and the Florida State University.

(2) R. S. Becker and M. Kasha, "Luminescence Spectroscopy of Molecules and the Photosynthetic System," Conference on Luminescence, Pacific Grove, California, March 29, 1954, National Research Council Bulletin, in press.