(1-Hydroxycyclopentyl)phenylcarbinol (2).—Similar treatment of benzaldehyde and cyclopentanone followed by several recrystallizations from benzene–petroleum ether yielded a material with m.p. 91–92.5° which could not be further purified by this method. Chromatography on alumina was likewise unsuccessful. Gas chromatography of the pinacol rearrangement product of this material indicated that cyclopentylcyclopentane-1,1'-diol was the contaminant. The mixture was separated by treatment with phthalic anhydride in pyridine.[19] The glycol thus purified had a m.p. of 81–82° (lit.[5] m.p. 80°) and its rearrangement product contained only 2% of spiro[4.5]decan-6-one (gas chromatography).

(1-Hydroxycyclohexyl)methylphenylcarbinol (3).—Acetophenone and cyclohexanone yielded 41% of crude material which on recrystallization had a m.p. of 109–110° (lit. m.p. 107.5–108,[20] 101.5,[19] 104°[18]).

(1-Hydroxycyclopentyl)methylphenylcarbinol (4).—Acetophenone and cyclopentanone yielded 37% of crude material which on recrystallization had a m.p. of 108.5–109°.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74. Found: C, 75.91; H, 8.78.

Independent Synthesis of Rearrangement Products.—Authentic samples of the rearrangement products of glycols 1–4 were prepared by known methods. This work is summarized in Table II. Purity of all samples was checked by gas chromatography and was over 90% except as noted.

The Rearrangement.—Concentrated sulfuric acid (96%) was cooled to 0° and the glycol (1 g./100 ml. of acid) was added in portions with stirring. When solution was complete, the reaction was poured into a mixture of ice and water (10 vol. of water/1 vol. of acid). When an organic layer separated it was taken off and the aqueous layer was extracted three times with ether. The combined ether layers were dried over magnesium sulfate; the ether was removed on the rotary evaporator. The crude residue was subjected to gas chromatography. Identifications were made by comparison with authentic samples; infrared spectra supplemented the analysis. Gas chromatographic analysis of synthetic mixtures of known composition showed that the method was reliable. Each rearrangement was done in duplicate; the average is reported in Table I. By treating all the measurements together the standard deviation was estimated to be 4%.

(19) C. A. Russell, L. T. Stroup, and J. English, Jr., *J. Am. Chem. Soc.*, **74**, 3882 (1952).

(20) G. G. Lyle, R. A. Covey, and R. E. Lyle [*ibid.*, **76**, 2713 (1954)] rearranged this compound with the same results obtained in the present work.

Structure of Neo-β-amyrin[1]

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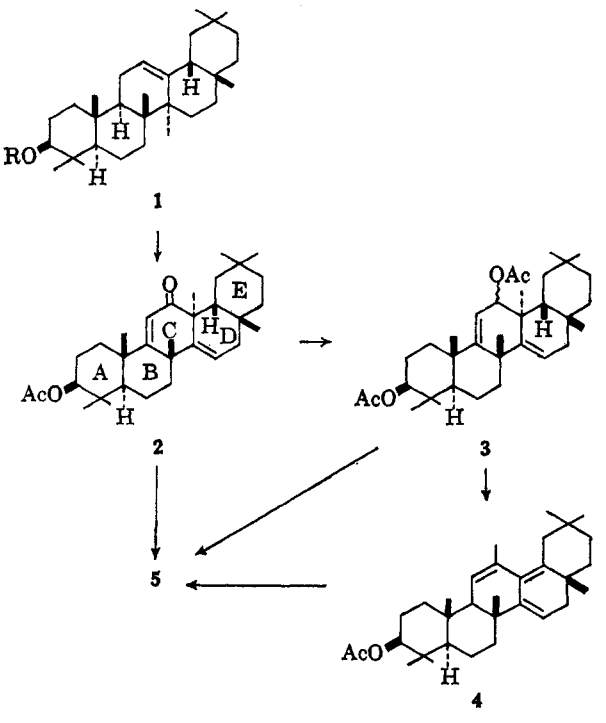
The reactions leading from β-amyrin acetate to neo-β-amyrin acetate have been re-examined, and structures based on C-nor-D-homooleanane are proposed for neo-β-amyrin and precursors.

There has been obtained from β-amyrin (**1**, R = H) by sequences of reactions involving at least two molecular rearrangements, an isomer which has been named neo-β-amyrin by Spring and co-workers.[2] In any of these sequences, the key intermediate is a dienone (**2**) (Chart I), prepared from β-amyrin acetate in three steps involving consecutive oxidation by (i) hydrogen peroxide in acetic acid to give the saturated 12-ketone[3–5]; (ii) bromine to yield the conjugated 9(11)-en-12-one[5,6]; and (iii) selenium dioxide[7] with methyl group migration from C-14 to C-13. The structure of the dienone **2**, which was first proposed by Jeger and Ruzicka,[8] is now well established.[2,9] In current nomenclature,[10] the dienone **2** is named 3β-acetoxy-D-friedooleana-9(11),14-dien-12-one; it has also been known variously as iso-β-amyradienonyl acetate,[7] oxoiso-β-amyradienyl acetate,[2] 12-oxoisooleana-9(11),-14-dien-3β-yl acetate,[11] and 12-oxotaraxera-9(11),14-dien-3β-yl acetate.[11]

Reduction of the dienone **2** with lithium aluminum hydride[2,6] or with sodium methoxide[2] in methanol at 200° yielded a dienediol, which was characterized as the diacetate and formulated as **3**, with unassigned configuration at C-12. Treatment of this diacetate with hydrochloric acid resulted in deacetoxylation with formation of a cross-conjugated triene (neo-β-amyratrienyl acetate) which Spring and colleagues[2] provisionally formulated as **4**. The production of a

CHART I



(1) The award of a research grant (AM-3439) from the U. S. Public Health Service (to R. S.) is gratefully acknowledged.

(2) G. G. Allan, J. D. Johnston, and F. S. Spring, *J. Chem. Soc.*, 1546 (1954).

(3) F. S. Spring, *ibid.*, 1345 (1933).

(4) L. Ruzicka, G. Müller, and H. Schellenberg, *Helv. Chim. Acta*, **22**, 758 (1939).

(5) C. W. Picard, K. S. Sharples, and F. S. Spring, *J. Chem. Soc.*, 1045 (1939).

(6) R. Budziarek, J. D. Johnston, W. Manson, and F. S. Spring, *ibid.*, 3019 (1951).

(7) J. Green, N. Mower, C. W. Picard, and F. S. Spring, *ibid.*, 527 (1944).

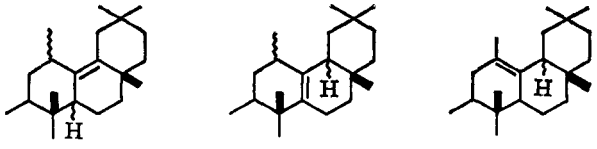
(8) O. Jeger and L. Ruzicka, *Helv. Chim. Acta*, **28**, 209 (1945).

(9) A. Meisels, O. Jeger, and L. Ruzicka, *ibid.*, **33**, 700 (1950).

(10) S. Allard and G. Ourisson, *Tetrahedron*, **1**, 277 (1957).

(11) J. M. Beaton, F. S. Spring, R. Stevenson, and J. L. Stewart, *J. Chem. Soc.*, 2131 (1955).

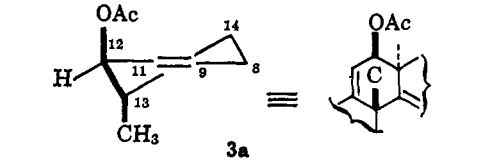
cross-conjugated triene system from **3** necessitates a molecular rearrangement, for which this proposal, involving a migration of methyl group from C-13 to C-12, is the most obvious. Catalytic hydrogenation of neo-β-amyratrienyl acetate resulted in the uptake of 2 moles of hydrogen yielding neo-β-amyrin acetate (**5**), the ultraviolet absorption spectrum of which indicated that the ethylenic bond present was tetrasubstituted; alternative structures (**5a** and **5b**) were consequently suggested as the most probable representations of neo-β-amyrin acetate, although the additional possibility (**5c**) does not seem to have been excluded.



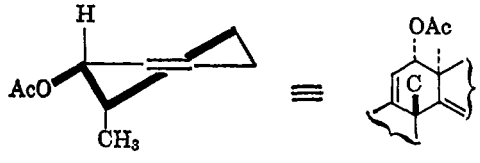
5a **5b** **5c**

It is also of interest that **5** is produced by catalytic reduction of both the dienone **2** and the diacetate **3**; it was further noted[2] that these hydrogenolyses were facilitated by the presence of hydrochloric acid and probably proceeded *via* the triene **4**.

If the principle of limitation applied to ionic rearrangements in cyclohexane systems[12] is valid for the unsaturated ring C in **2**, the pertinent atoms (the 13α-methyl C atom, C-13, C-12, and the O atom attached to C-12) involved in the postulated **3** → **4** rearrangement should be coplanar, with the departing acetate group and moving methyl group *trans* and antiparallel; *i.e.*, the 12-acetate group should have the β configuration and quasi-axial conformation (**3a**). By the methods of preparation of the diacetate **3**, which involved reduction of the 12-ketone group, we considered that the 12-acetate should have the more stable quasi-equatorial conformation and hence α configuration (**3b**). In this event, consideration of stereoelectronic principles indicated that an alternative rearrangement, involving migration of the C-13,14 bond to C-12 to produce a C-nor-D-homo system, is likely and that **6** should be considered as the structure for neo-β-amyratrienyl acetate. A similar C-nor-D-homo rearrangement, but with the D-ring enlarging from five- to six-membered, is well known in steroid systems,[13-15] being effected by solvolysis of equatorial sulfonate esters at C-12, and a similar conversion of a 1-hydroxytriterpene into an A-nor-B-homotriterpene has recently been reported.[16]



3a



3b

We sought initially to obtain evidence for our belief that the diene diacetate **3** has the 12α-acetate configuration (**3b**). By measurement from Dreiding models, the H-11–C-11–C-12–H-12α dihedral angle is *ca.* 30° in the 12-quasi-axial epimer (**3a**) and a relatively high coupling (6–8 c.p.s.) would be predicted for the C-11 olefinic proton signal. In the 12-quasi-equatorial epimer (**3b**), the corresponding H-11–C-11–C-12–H-12β dihedral angle is *ca.* 90° and a low coupling constant (0–2 c.p.s.) is expected.[17] An examination of the proton magnetic resonance spectrum of the diene diacetate reveals the presence, as expected, of two olefinic protons. The signal due to the C-15 proton is a quartet centered at δ 5.70, and that of the C-11 proton is a doublet at δ 5.43 (J = 2 c.p.s.). In addition, the signals due to the C-3 and C-12 protons are evident, the former as a broad multiplet at δ 4.45 and the latter as a doublet at δ 5.17 (J = 2 c.p.s.). We consequently consider that the diene diacetate has the structure 3β,12α-diacetoxy-D-friedooleana-9(11),14-diene (**3b**).

The conversion of **3b** to neo-β-amyratrienyl acetate by the action of hydrochloric acid in acetic acid at room temperature was described by Allan, *et al.*[2] We have repeated this, following the course of the reaction by thin layer chromatographic examination of aliquot fractions. The optimum time for triene production was found to be 7 hr., and, under these conditions, neo-β-amyratrienyl acetate could be isolated in about 70% yield.

A distinction between the two most likely structures, **4** and **6**, for the trienyl acetate was sought in examination of the n.m.r. spectrum. Both **4** and **6** require the presence of two vinyl protons and one vinyl methyl group. In either case, the vinyl proton at C-15 should give a quartet signal by coupling with the 16-methylene group. The remaining vinyl proton at C-11 should give, in formulation **4**, a multiplet by coupling with the C-9 proton (low J value) and possibly the methyl group protons at C-12; in contrast, a singlet signal would be expected for the C-11 proton in formulation **6**. It might be further anticipated that the signal due to the protons of the 12-methyl group in **4** might be a doublet due to coupling with the H-11 proton, but that attributable to the corresponding 13-methyl group in **6** would be a singlet (or broad singlet due to coupling with the C-18 proton). Since the appropriate signals in the 100-Mc. spectrum are in fact both singlets (at δ 5.90 for the C-11 vinyl proton and δ 1.88 for the vinyl methyl group), we interpret this evidence as favoring the C-nor-D-homo formulation (**6**).

Catalytic hydrogenation of neo-β-amyratrienyl acetate in acetic acid solution gave neo-β-amyrin acetate with empirical constants in good agreement with those previously reported.[2] We have also confirmed the hydrogenolysis with rearrangement of the dienone

(12) D. H. R. Barton, J. Chem. Soc., 1027 (1953).

(13) R. F. Hirschmann, C. S. Snoddy, C. F. Hiskey, and N. L. Wendler, *J. Am. Chem. Soc.*, **76**, 4013 (1954).

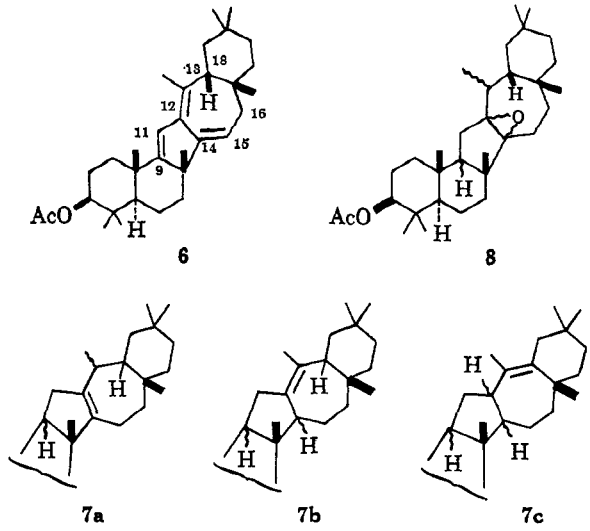
(14) J. Elks, G. H. Phillips, D. A. H. Taylor, and L. J. Wyman, *J. Chem. Soc.*, 1739 (1954).

(15) J. M. Coxon, M. P. Hartshorn, and D. N. Kirk, *Tetrahedron Letters*, 119 (1965).

(16) S. Huneck, *ibid.*, 1977 (1963).

(17) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p. 50.

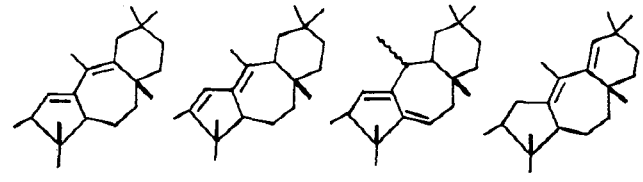
CHART II

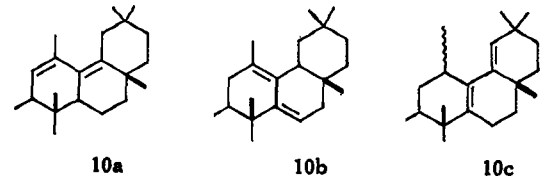


2 and diene diacetate **3b** to neo-β-amyrin acetate. If the previous evidence, based on the ultraviolet absorption between 210 and 225 mμ, that the double bond present in neo-β-amyrin acetate is tetrasubstituted, three possible structures, **7a**, **7b**, and **7c** (Chart II), based on the C-nor-D-homo skeleton, present themselves. The n.m.r. spectrum of neo-β-amyrin acetate confirms the absence of vinyl protons. Since, furthermore, there is no signal indicative of a vinyl methyl group present, structures **7b** and **7c** (also **5c**) are excluded, and structure **7a** is suggested for neo-β-amyrin acetate.

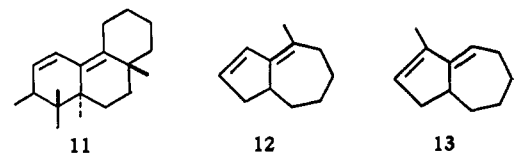
It was previously established that oxidation of neo-β-amyrin acetate with chromic acid, potassium permanganate, or perbenzoic acid gave an oxide, which on treatment with hydrochloric acid yielded a conjugated diene.[2] We have re-examined these two reactions. The oxide, now formulated as **8**, was obtained with constants in good agreement with those previously reported and in higher yield, by oxidation with both *m*-chloroperbenzoic acid and chromic acid. The acid-catalyzed cleavage and dehydration of the oxide to yield neo-β-amyradienyl acetate was improved by curtailing the reaction time from 18 hr. to 10 min. We have further obtained evidence that no molecular rearrangement occurred during this acid-catalyzed oxide opening. Thus, when neo-β-amyradienyl acetate was treated with 1 molar equiv. of *m*-chloroperbenzoic acid and the reaction mixture was chromatographed, neo-β-amyratrienyl acetate was isolated in about 40% yield.

The ultraviolet absorption spectrum of neo-β-amyradienyl acetate [257 mμ (ε 19,000)] indicates that it is a conjugated *transoid* heteroannular diene. On the C-nor-D-homo formulation (**7a**) of the parent system, four structures (**9a–d**) can be written satisfying this requirement, while on the tentative Spring formulation (**5a** or **5b**), three structures (**10a–c**) can be considered. The n.m.r. spectrum of neo-β-amyradienyl acetate indicated the presence of only *one* vinyl hydrogen and *one* vinyl methyl group, thus excluding structures **9c** and **10c**. Furthermore, since the signal due to the vinyl proton is a doublet (δ 5.70, J = 5 c.p.s.), this indicates that it is adjacent to a methine group, thus eliminating **9b**, **9d**, and **10c**. Of the two remaining





possibilities, **9a** and **10a**, the observation that the vinyl methyl signal (δ 1.72) is unsplit supports structure **9a**. The ultraviolet absorption spectrum can also be interpreted as favoring **9a** over **10a**. Conjugated heteroannular dienes in which only cyclohexane rings are involved show fine structure at the ultraviolet maximum absorption wave length usually consisting of a maximum with subsidiary peaks or shoulders at either side, separated from the principal maximum by about 8 mμ. For example, this pattern is shown by the $\Delta^{3,5}$, $\Delta^{4,6}$, and $\Delta^{7,9(11)}$ steroid dienes,[18] by the $\Delta^{7,9(11)}$-lanostadienes and -euphadienes, and most significantly by $\Delta^{11,13,(18)}$-oleanadienes and -ursadienes (part structure **11**). We suggest that, since this fine structure



maximum is not shown in the ultraviolet absorption spectrum of neo-β-amyradienyl acetate, structure **10a** is an unlikely representation.[19] Ultraviolet absorption data regarding heteroannular diene systems in which the chromophore is located in adjoining cyclopentane and cycloheptane rings is appreciably more scarce. In agreement, however, single-peak maxima are reported for the naturally occurring sesquiterpenoid matricin[20] [λ 247 mμ (log ε 4.32)] which has part structure **12** and some oxidation products [λ 242–243 mμ (ε 16,300–20,800)] with part structure **13**, derived from α-gurjunene.[21] The wave length (257 mμ) of maximum absorption of neo-β-amyradienyl acetate is also reasonable for structure **9a**, which has, in comparison with **12** and **13**, an additional ring alkyl substituent and two exocyclic double-bond increments.

(18) Summaries of steroid conjugated diene absorption spectra are given by (a) L. Dorfman, *Chem. Rev.*, **53**, 47 (1953); (b) J. P. Dusza, M. Heller, and S. Bernstein, "Physical Properties of the Steroid Hormones," L. L. Engel, Ed., The Macmillan Co., New York, N. Y., 1963, pp. 69–287; (c) A. I. Scott, "Interpretation of Ultra-Violet Spectra of Natural Products," The Macmillan Co., New York, N. Y., 1964, Chapter 2. It is of possible significance that the steroid $\Delta^{5,5(14)}$- and $\Delta^{5,14}$-dienes which do not give three maxima absorption have a double bond *exo* or *endo* to a cyclopentane ring.

(19) The effects of a methyl group on the diene chromophore results in a bathochromic shift; *cf.* cholesta-3,5-diene (228, 235, and 243 mμ) and 3-methylcholesta-3,5-diene (232, 239, and 248 mμ).

(20) M. Suchy, V. Herout, and F. Sorm, *Collection Czech. Chem. Commun.*, **29**, 1829 (1964). An earlier reported value of λ 244 mμ (log ε 4.22) was given by Z. Cekan, V. Herout, and F. Sorm, *ibid.*, **19**, 798 (1954).

(21) J. Streith and G. Ourisson, *Bull. soc. chim. France*, 1960 (1963).

We conclude, on the basis of all available evidence, that neo-β-amyrin has the structure 13-methyl-27-nor-C-nor-D-homoolean-12(14)-en-3β-ol (**7a**, R = H).[22]

Experimental Section

Specific rotations were determined in chloroform solution, and ultraviolet absorption spectra were measured in ethanol solution. All melting points were determined using a Gallenkamp melting point apparatus. N.m.r. spectra were determined in deuteriochloroform solution with tetramethylsilane as an internal standard using Varian spectrophotometers (4300B, A-60, and HA-100). Thin layer chromatographic examinations were performed using Merck silica gel G as absorbent, benzene–chloroform (1:1) as developing solvent, and iodine vapor as detecting agent. Petroleum ether refers to the fraction of b.p. 30–60°.

3β,12α-Dihydroxy-D-friedooleana-9(11),14-diene.—A solution of 3β-acetoxy-D-friedooleana-9(11),14-dien-12-one (iso-β-amyradienonyl acetate[6]) (1.2 g.) in dry ether (250 ml.) was heated under reflux for 4 hr. with excess lithium aluminum hydride. One crystallization of the product, isolated in the usual way, from methylene chloride–methanol gave the dienediol as needles: m.p. 196–198°, $[\alpha]_D$ −16° (*c* 1.1); lit.[2] m.p. 202–204°, $[\alpha]_D$ −17°.

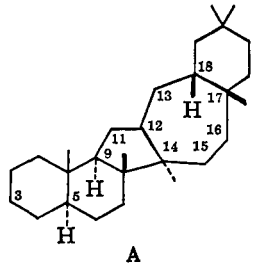
3β,12α-Diacetoxy-D-friedooleana-9(11),14-diene.—A solution of the dienediol (800 mg.) in pyridine (10 ml.) and acetic anhydride (8 ml.) was heated on the steam bath for 3 hr. and worked up in the usual way, and the product was crystallized from aqueous methanol to give the diacetoxydiene as rectangular plates: m.p. 163–164°, $[\alpha]_D$ +24° (*c* 1.7); lit.[2] m.p. 167–168°, $[\alpha]_D$ +25°.

N.m.r. signals appeared at δ 0.88, 0.92 (sh), 0.96 (sh), 1.21, 1.28, 1.37 (methyl groups), 2.03, 2.10 (C-3 and C-12 acetoxyl protons), 4.45 (multiplet, 3α-H), 5.17 (doublet, J = 2 c.p.s., 12β-H), 5.43 (doublet, J = 2 c.p.s. 11-H), and 5.70 (pair of doublets, J = 2.5 c.p.s., J' = 6.5 c.p.s., 15-H).

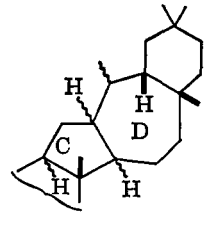
13-Methyl-27-nor-C-nor-D-homooleana-9(11),12,14-trien-3β-yl Acetate (Neo-β-amyratrienyl Acetate).—Concentrated hydrochloric acid (0.3 ml.) was added to a solution of the diacetoxydiene (50 mg.) in acetic acid (4 ml.) at room temperature. Within 5 min., a crystalline solid had separated. After 7 hr., the mixture was diluted with water; the precipitate was collected by filtration, dissolved in petroleum ether, and chromatographed on alumina (Savory and Moore). Elution with the same solvent gave the trienyl acetate (30 mg.) which crystallized from methylene chloride–methanol as thick needles: m.p. 163–164°; $[\alpha]_D$ +57° (*c* 1.2); λ 228 mμ (ε 17,000), 282 (15,000), and 294 (11,500); lit.[2] m.p. 168–169°, $[\alpha]_D$ +58°. It gives a purple color with tetranitromethane in chloroform solution.

N.m.r. signals were at δ 0.82, 0.88, 0.91, 0.94, 1.15, and 1.24 (methyl groups), 1.88 (C-13 methyl protons), 2.05 (C-3 acetoxyl protons), 4.45 (multiplet, 3α-H), 5.30 (pair of doublets, J = 2 c.p.s., J' = 7 c.p.s., 15-H), and 5.90 (11-H).

(22) The nomenclature and numbering proposed is based on C-nor-D-homooleanane (A). The structures proposed for compounds in the neo-β-amyrin group are, consequently, named as derivatives of 13-methyl-27-nor-C-nor-D-homooleanane (B) with unassigned configuration at C-9, -12, -13, and -14.



A



B

13-Methyl-27-nor-C-nor-D-homoolean-12(14)-en-3β-yl Acetate (Neo-β-amyrin Acetate). A.—A solution of neo-β-amyratrienyl acetate (78 mg.) in acetic acid (25 ml.) was stirred under hydrogen at atmospheric pressure and temperature for 4 hr. with platinum (prereduced from 56 mg. of PtO_2). Crystallization of the residue, obtained after filtration and evaporation of solvent, from methylene chloride–methanol gave neo-β-amyrin acetate as long needles: m.p. 224–225°, $[\alpha]_D$ +7°; lit.[2] m.p. 225–227°, $[\alpha]_D$ +6°. N.m.r. signals were at δ 0.82, 0.88, 0.92, 1.02, 1.11, and 1.13 (methyl groups) and 1.93 (C-3 acetoxyl protons).

B.—Similar catalytic hydrogenation of iso-β-amyradienonyl acetate in cyclohexane–acetic acid and iso-β-amyradienediol diacetate in acetic acid, both with 2 drops of concentrated hydrochloric acid added, gave neo-β-amyrin acetate, m.p. 223–224°.

12(14)-Oxido-13-methyl-27-nor-C-nor-D-homooleanan-3β-yl Acetate (Neo-β-amyrin Acetate Oxide). A.—A solution of chromium trioxide (25 mg.) in water (few drops) and acetic acid (8 ml.) was added dropwise over 10 min. to a solution of neo-β-amyrin acetate (50 mg.) in acetic acid (5 ml.). The mixture was then heated at 100° for 90 min., cooled, poured into water, and extracted with ether. The extract was washed with water, sodium hydrogen carbonate solution, and water and dried ($MgSO_4$). The residue obtained on evaporation was dissolved in benzene, chromatographed on Merck alumina (4 g.), and eluted with benzene to give a fraction (35 mg.) which on crystallization from methanol yielded neo-β-amyrin acetate oxide as needles: m.p. 207–209°, $[\alpha]_D$ −6° (*c* 0.8); lit.[2] m.p. 203.5–204.5°, $[\alpha]_D$ −4°.

B.—A solution of *m*-chloroperbenzoic acid (45 mg.) in chloroform (3 ml.) was added to a solution of neo-β-amyrin acetate (50 mg.) in chloroform (5 ml.), and the mixture was allowed to stand at room temperature for 2 hr. Potassium iodide was then added, and the solution was washed successively with dilute sodium thiosulfate solution, water, dilute sodium hydrogen carbonate solution, and water. The chloroform extract, after drying, was evaporated and the residue (36 mg.) was crystallized from methanol to give neo-β-amyrin acetate oxide, m.p. 205–206°.

13-Methyl-27-nor-C-nor-D-homooleana-11,13(18)-dien-3β-yl Acetate (Neo-β-amyradienyl Acetate).—Concentrated hydrochloric acid (0.8 ml.) was added to a solution of neo-β-amyrin acetate oxide (50 mg.) in chloroform (1 ml.) and acetic acid (7 ml.); the mixture was kept at room temperature for 10 min. then poured into water and extracted with ether. The extract was worked up in the usual way and the residual product was dissolved in petroleum ether and chromatographed on alumina (4 g., Savory and Moore). Elution with the same solvent afforded neo-β-amyradienyl acetate (25 mg.), which crystallized from methylene chloride–methanol as long needles: m.p. 192–193°, $[\alpha]_D$ −35° (*c* 0.87), λ 257 mμ (ε 19,000); lit.[2] m.p. 192–194°, $[\alpha]_D$ −3°. N.m.r. signals were at δ 0.87, 1.00, 1.15 (methyl groups), 1.72 (C-13 methyl protons), 2.02 (C-3 acetoxyl protons), 4.47 (multiplet, 3α-H), and 5.70 (doublet, J = 5 c.p.s., 11-H).

Conversion of Neo-β-amyradienyl Acetate to Neo-β-amyratrienyl Acetate.—A solution of *m*-chloroperbenzoic acid (40 mg.) in chloroform (2 ml.) was added to a solution of neo-β-amyradienyl acetate (50 mg.) in chloroform (5 ml.). After 5 min., when all the peracid had been consumed, water was added and the chloroform layer was separated, washed in the usual way, and evaporated. The residual oil was dissolved in petroleum ether and chromatographed on alumina (5 g., Merck acid washed). Elution with the same solvent gave neo-β-amyratrienyl acetate (15 mg.), identified by comparison with an authentic specimen. Further elution yielded oils, shown by thin layer chromatography to be mixtures.

In another experiment, in which the product was chromatographed on Florisil, the diene (50 mg.) yielded the triene (17 mg., m.p. 163–165°).

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