Attempted Chlorination of Acetaldehyde.—Sulfuryl chloride (27 g., 0.2 mole) was added slowly to acetaldehyde (8.8 g., 0.2 mole) which was cooled in an ice bath. The first few drops of sulfuryl chloride caused the reaction temperature to rise from 5 to 25°. After cooling the reaction mixture again to 5°, the addition of the rest of the sulfuryl chloride did not cause an increase in temperature of the reaction mixture. The viscous light yellow liquid was allowed to stand overnight at room temperature, and then it was distilled. Sulfuryl chloride (18 g.) was recovered. A fraction with b.p. 121–124° (2 g., 23%) was recovered. Its infrared spectrum showed no carbonyl absorptions at 5.5–6.0, but had an intense ether band at 9.5 μ. The n.m.r. spectrum of this compound had a complex series of methyl transitions at τ ~9. This material was identical with authentic paraldehyde (b.p. 124°). The viscous residue (mol. wt. 570, Mechrolab vapor pressure osmometer) which remained had infrared and n.m.r. spectra which were similar to the above and, on this basis and elemental analysis, was assigned the structure of a low molecular weight linear polymer.

Anal. Calcd. for $(C_2H_4O)_n$: C, 54.6; H, 9.1. Found: C, 53.9; H, 8.7; Cl, 1.31.

Chlorination of Propionaldehyde.—Sulfuryl chloride (1.9 mole) and anhydrous sodium carbonate (1 mole) were placed in the usual apparatus and well stirred while propionaldehyde (2 moles) was slowly added over a period of ~40 min. Occasional cooling with an ice bath was necessary to moderate the reaction. As soon as the addition was complete, ice–water was added in sufficient quantity (~500 ml.) to rapidly dissolve all of the salts. The organic layer was separated and washed with 500 ml. of 5% aqueous sodium carbonate and then water. After drying over anhydrous calcium chloride the viscous residue was subjected to distillation using a water bath as heat source. After removal of a small amount of forerun there was obtained 4.0 g. of a colorless liquid, b.p. 84° at atmospheric pressure. The n.m.r.[19] spectrum (neat liquid) consisted of a doublet, τ 8.4, and a multiplet, τ 5.75, which, as a first approximation, was a quartet split by coupling with another proton. The elemental analysis was correct for α-chloropropionaldehyde.

Anal. Calcd. for C_3H_5ClO: C, 38.9; H, 5.4; Cl, 38.4. Found: C, 38.2; H, 5.4; Cl, 38.3.

Upon standing in the dark in the refrigerator overnight the liquid solidified to colorless crystals, which in 2 days began to darken. After 1 week in the refrigerator the solid had been completely converted to a brownish oil (mol. wt. 265, Mechrolab vapor pressure osmometer). The molecular weight was approximately correct for cyclic trimer (theoretical mol. wt. 277). Most of the product from the attempted chlorination was a low molecular weight, viscous polymer which could not be distilled.

Chlorination of Isobutyraldehyde.—The procedure used was identical with that described above for the chlorination of propionaldehyde. From 1 mole each of isobutyraldehyde and sulfuryl chloride reacted in the presence of 0.75 mole of anhydrous sodium carbonate, there was obtained 5 g. of α-chloroisobutyraldehyde, b.p. 36° at 240 mm. The n.m.r. spectrum consisted of a singlet, τ 8.35. The colorless liquid crystallized when stored overnight in the refrigerator, but the crystals were soon converted into a brown liquid (mol. wt. 800, Mechrolab vapor pressure osmometer). Interestingly, the result which indicates a number average degree of polymerization of 8, implies that α-chloroisobutyraldehyde, unlike α-chloropropionaldehyde (see above), prefers to polymerize linearly rather than trimerize into a cyclic compound.

Most of the product from the reaction of isobutyraldehyde with sulfuryl chloride was a low molecular weight polyether. Neither the polyether or the volatile product described above showed carbonyl bands (5.5–6.0 μ) in their infrared spectra.

(19) The chemical shift of the proton in the CHO group (a doublet) occurred at $\tau \approx 0.1$ (*cf.* L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 62).

Acknowledgment.—We are indebted to Mr. Carl Lindemann for the gas chromatograph results.

The Action of Alumina on α- and β-Amyrin Sulfonate Esters[1]

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Filtration of α-amyrin sulfonate ester solutions through neutral alumina results in elimination of the sulfonic acid and formation of a product $C_{30}H_{48}$, "α-amyradiene-IV," previously reported, by the action of boiling pyridine on α-amyrin methanesulfonate. It is shown that "α-amyradiene-IV" is a mixture of ursa-2,12-diene and 3ξ-methyl-24-norursa-4(23),12-diene. Under the same conditions of alumina or tertiary base treatment, β-amyrin sulfonate esters behave in analogous fashion.

Dehydration of the pentacyclic triterpenoid alcohols, α-amyrin (urs-12-en-3β-ol) (**1**, R = H) and β-amyrin (olean-12-en-3β-ol) (**2**, R = H), and related elimination reactions of their ester derivatives have given rise to a variety of diene structural isomers.[2,3] By brief treatment with phosphorus pentachloride, α-amyrin and β-amyrin give, respectively, A-neoursa-3,12-diene (α-**3**)[4–7] and A-neooleana-3,12-diene (β-**3**)[4,6,8,9] which, on prolonged exposure to phosphorus pentachloride or isomerization with trichloroacetic acid, are converted to the corresponding isomers, A-neoursa-3(5),12-diene (α-**4**)[7] and A-neooleana-3(5),12-diene (β-**4**).[9] The benzoate esters (**1**, R = Bz) and (**2**, R = Bz) on pyrolysis behave similarly to yield ursa-2,12-diene (α-**5**)[8] and oleana-2,12-diene (β-**5**).[8,10] These transformations, a retropinacolic dehydration and a thermal *cis* elimination, have been rationalized in terms of conformation theory[11] and are amply documented in related systems.

In view of the close structural relationship of **1** and **2** (differing only in methyl substitution in ring E), it is at first sight surprising that there should be noteworthy differences in their elimination behavior under identical conditions; two such reports, however, exist. By treat-

(1) The award of a research grant (AM-3439) from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service (to R. S.), is gratefully acknowledged.

(2) Apart from trivial names assigned to these isomers prior to their structure elucidation, the nomenclature used in this paper is that proposed by S. Allard and G. Ourisson [*Tetrahedron*, **1**, 277 (1957)] after consultation with authorities in this field.

(3) To conserve space in the structure formulations, the prefixes α- and β- before formula numbers refer to α-amyrin (ursane) and β-amyrin (oleanane) derivatives, respectively.

(4) A. Vesterberg, *Ber.*, **20**, 1242 (1887).

(5) K. A. Vesterberg and S. Westerlind, *Ann.*, **428**, 247 (1922).

(6) L. Ruzicka, H. Silbermann, and M. Furter, *Helv. Chim. Acta*, **15**, 482 (1932).

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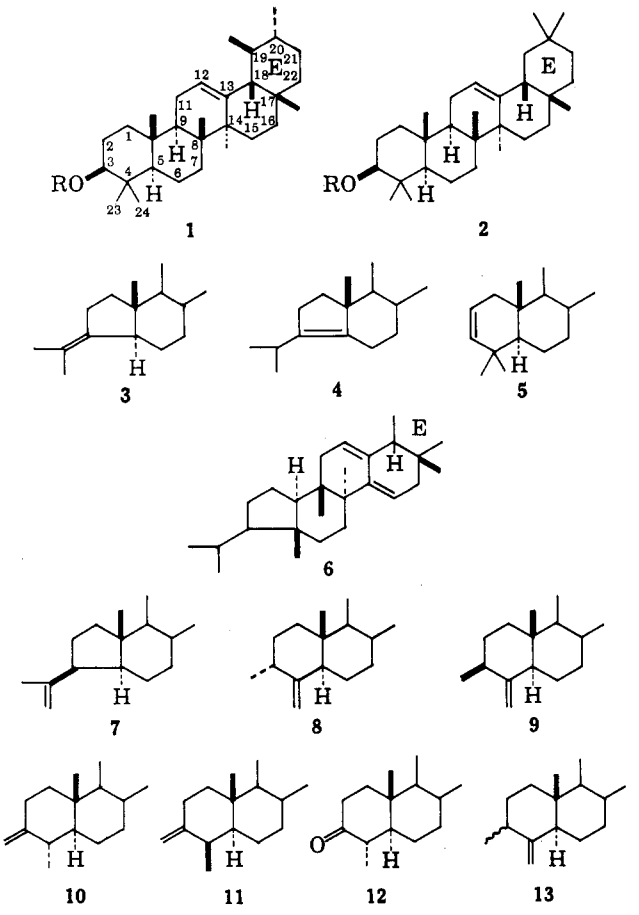
(11) D. H. R. Barton and G. A. Morrison, "Fortschritte der Chemie Organischer Naturstoffe," Vol. 19, Springer-Verlag, Vienna, 1961.



ment of α-amyrin with phosphorus pentoxide, Vesterberg[12] isolated the so-called *l*-α-amyradiene; this could also be isolated by the action of hydriodic acid on **1** (R = H or Ac), and was shown to be conjugated[13] and to have the structure A:D-neoursa-12,14-diene (α-**6**).[14] The failure of β-amyrin to undergo this remarkable transformation, involving ring contraction and a succession of six 1,2-shifts of hydride and methyl groups, has been attributed to the instability in acid media of the *cis* D–E ring fusion in the oleanane series, in contrast to the ursane series. The analog (β-**6**) has indeed been obtained by a circuitous route in which isomerization at C-18 was prevented.[9]

The second difference in behavior of α- and β-amyrin, which must be due to some other cause, was reported in a brief communication by Noller and Hearst[15] and deals with the stability of the methanesulfonate esters towards boiling pyridine solution. Whereas β-amyrin methanesulfonate (**2**, R = CH_3SO_2–) gave oleana-2,12-diene (β-**5**), there was obtained from α-amyrin methanesulfonate (**1**, R = CH_3SO_2–) under the same conditions a diene, $C_{30}H_{48}$, named "α-amyradiene-IV" which differed from α-**3**, α-**4**, α-**5**, and α-**6**. We chose to reinvestigate this reaction, for which no experimental details were given, for the purposes of deriving the structure of "α-amyradiene-IV" and explaining the failure of β-amyrin to form an analogous "β-amyradiene-IV."

(12) A. Vesterberg, *Ber.*, **24**, 3834 (1891).
(13) E. S. Ewen, A. E. Gillam, and F. S. Spring, *J. Chem. Soc.*, 28 (1944).
(14) M. B. E. Fayez, J. Grigor, F. S. Spring, and R. Stevenson, *ibid.*, 3378 (1955).
(15) C. R. Noller and P. J. Hearst, *J. Am. Chem. Soc.*, **72**, 625 (1950)

In our experience, when a pyridine solution of α-amyrin methanesulfonate is heated under reflux for periods up to 10 hr., unchanged ester can readily be recovered by solvent removal and direct crystallization of the reaction mixture. The reported failure of Burns, *et al.*,[16] to prepare "α-amyradiene-IV" is probably largely explicable by the short reaction time (5 hr.) which they employed. When longer periods (2–7 days) of reflux were employed, and the reaction products isolated by alumina column chromatography followed by repeated recrystallization of the hydrocarbon fraction, "α-amyradiene-IV", with constants in good agreement with those previously reported,[15] was obtained in yields up to 50%.[17] We have now shown that the *same* hydrocarbon is readily obtained by simple chromatography of the methane- or toluenesulfonate esters on Woelm neutral alumina *without* prior heating in pyridine, and is the obvious preparative method of choice. That the elimination does indeed occur during pyridine treatment, as well as on alumina, we have established by infrared examination of crude total fractions, withdrawn from the reaction at time intervals, and worked up without chromatographic treatment; the disappearance of sulfonate ester and hydrocarbon formation is essentially complete after 3 days.

The presence of an intense band in the 890-cm.$^{-1}$ region of the infrared spectrum of "α-amyradiene-IV" indicated the presence of a vinylidene group, a conclusion substantiated by the isolation of formaldehyde, as its dimedone derivative, after ozonolysis or osmium tetroxide oxidation followed by lead tetraacetate treatment. The low yield of formaldehyde obtained, together with the presence also of an infrared band at 730 cm.$^{-1}$ (characteristic of a disubstituted double bond[18]) in "α-amyradiene-IV," suggested the possibility that the apparently homogeneous crystalline hydrocarbon was a mixture. The complexity of the n.m.r. spectrum in both the vinyl and methyl proton regions supported this likelihood. Although we were unable to separate "α-amyradiene-IV" into separate constituents by careful chromatography on alumina, a highly efficient separation into two components was achieved by thin layer chromatography on silica gel impregnated with silver nitrate.[19] In this manner, "α-amyradiene-IV," m.p. 126–128°, $[\alpha]_D$ +150°, yielded, in approximately equal amounts, the product of higher R_f value, m.p. 114–115°, $[\alpha]_D$ +135°, identified as ursa-2,12-diene (α-**5**) and a product of lower R_f, m.p. 155–156°, $[\alpha]_D$ +169°, which we regard as pure α-amyradiene-IV.[20]

Treatment of α-amyradiene-IV with trichloroacetic acid in chloroform solution at room temperature yielded a mixture of isomers which was examined by the thin layer technique, and of which one component was identified as *l*-α-amyradiene (α-**6**). Under the same conditions, ursa-2,12-diene was recovered unchanged. This rearrangement, taken in conjunction with the presence

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(17) M. B. E. Fayez, F. S. Spring, and R. Stevenson, unpublished observations.
(18) A. R. H. Cole and D. W. Thornton, *J. Chem. Soc.*, 1332 (1957).
(19) C. B. Barrett, M. S. J. Dallas, and F. B. Padley, *Chem. Ind.* (London), 1050 (1962).
(20) In this paper, "α-amyradiene-IV" refers to the previously described[15] product now shown to be a mixture of ursa-2,12-diene and α-amyradiene-IV.

of a vinylidene group in α-amyradiene-IV, suggested that α-**7** was the most likely structure representation. Catalytic hydrogenation of α-amyradiene-IV resulted, however, in reduction of the vinylidene group, to yield a product differing from those obtained by similar reduction of α-**3**.[6,8] The doubt which this cast on the validity of α-**7** for the structure was confirmed by consideration of the n.m.r. spectrum of α-amyradiene-IV. This showed appropriate signals for three vinyl protons at δ 4.40 and 4.67 (methylene group) and 5.13 (C-12 proton), but lacked a methyl peak at the region of δ 1.7, characteristic of an allylic methyl group[21,22]; the postulated isopropenyl group in α-**7** is consequently untenable. This is further substantiated by examination of the n.m.r. spectrum of the crystalline ketone $C_{29}H_{46}O$, derived from α-amyradiene-IV by osmium tetroxide addition, followed by lead tetraacetate cleavage and base treatment; it showed the presence of one vinyl proton (δ 5.18, C-12) and the absence of a methyl ketone group.

With the exclusion of α-**7** as a structure for α-amyradiene-IV, α-**8**, α-**9**, α-**10**, and α,**11** can be regarded as the most likely formulations. Of these, 3-methylene-24-norurs-12-ene (α-**10**) is known,[23] having been prepared from nor-β-boswellelone (α-**12**), and differs from α-amyradiene-IV notably in the specific rotation value. The norketone obtained from α-amyradiene-IV by cleavage of the methylene group followed by base equilibration moreover differs from α-**12** and consequently excludes α-**10** and α-**11**. The present evidence does not permit an unequivocal distinction between the remaining probable structures, α-**8** and α-**9**, and until further evidence is available, we consider that α-amyradiene-IV should be regarded as 3ξ-methyl-24-norursa-4(23),12-diene (α-**13**).[24]

In the oleanane series, we find that filtration through neutral alumina of a solution of β-amyrin methanesulfonate (**2**, R = CH_3SO_2–) or toluenesulfonate (R = $CH_3C_6H_4SO_2$–) results in an elimination which parallels the behavior in the ursane series. The hydrocarbon mixture "β-amyradiene-IV," m.p. 134–135°, $[\alpha]_D$ +157°, was readily separated by thin layer chromatography into two components, one identified as oleana-2,12-diene (β-**5**), m.p. 145–147°, $[\alpha]_D$ +136°, and the other, β-amyradiene-IV, m.p. 167–169°, $[\alpha]_D$ +167°, for which the structure 3ξ-methyl-24-noroleana-4(23),-12-diene (β-**13**) is proposed. We find, however, in contrast to "α-amyradiene-IV" which we were unable to separate by recrystallization, that fractional crystallization of "β-amyradiene-IV" results in separation of oleana-2,12-diene (β-**5**) as the less soluble component of the mixture. This experience suggested an explanation of the apparently contrasting (and anomalous) behavior of the sulfonate esters of α- and β-amyrin on being boiled in pyridine solution, as indicated by Noller and Hearst.[15] In our hands, β-amyrin methanesulfonate, on treatment with pyridine in the exact manner employed in the ursane series, gave the hydrocarbon mixture "β-amyradiene-IV," but in this case oleana-2,-12-diene could be isolated directly by repeated crystallization from chloroform–methanol.

The reaction of toluenesulfonates, notably of steroids, with alumina to give hydrocarbon and alcohol mixtures has been reported, and in several cases it has been shown to have preparative utility, although the products and ratios can vary markedly with duration of reaction and alumina composition.[25–27] Under the conditions described by Douglas, *et al.*,[27] α-amyrin toluenesulfonate gave noncrystalline unsaturated material (75% yield) from which ursa-2,12-diene (α-**5**) could be isolated in 35% yield. The reported near identity of crude material with pure α-**5** would suggest the essential absence of α-amyradiene-IV (α-**13**). They also report the isolation of β-**5** by alumina treatment of β-amyrin toluenesulfonate without detection of β-**13**. It has also been noted[28] that lanost-8-en-3β-yl toluenesulfonate decomposed on alumina to give a hydrocarbon mixture, one constituent of which was lanosta-2,8-diene. It is suggested here that a by-product, which shows infrared absorption at 883 $cm.^{-1}$, is the rearranged lanostane analog of **13**.

It is intended to examine further the generality of this alumina-induced elimination with molecular rearrangement (**1** → **13**) in more readily available saturated systems, *e.g.*, 4,4-dimethylcholestanol, with a view to gaining an insight into the detailed stereochemistry of the methyl-group migration.

Experimental

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 CCl_4 or $CDCl_3$ solution with tetramethylsilane as an internal standard using Varian 4300B or A60 spectrophotometers. The thin layer chromatographic technique followed the directions previously described:[19] aqueous silver nitrate solution (12.5%, 60 ml.) was added to silica gel G (30 g., Merck), and the mixture was shaken to a slurry for 1 min. For analytical purposes, the slurry was applied to glass plates in a 0.25-mm. layer, and for preparative purposes in a 1.00-mm. layer. The plates were dried at room temperature for 30 min., then activated prior to use at 125° for 2 hr. Carbon tetrachloride was used as developing solvent.

"α-Amyradiene-IV." A.—A solution of α-amyrin methanesulfonate[29] (3.0 g., m.p. 120° dec., $[\alpha]_D$ +71°) in pyridine (150 ml.) was heated under reflux for 7 days and evaporated under reduced pressure; the residue was extracted with ether–benzene; and the extract was washed with water, dilute hydrochloric acid, sodium bicarbonate solution, and water. The dried extract was dissolved in petroleum ether (b.p. 40–60°) and filtered through alumina (Woelm, neutral, grade I). The eluate (250 ml.) was evaporated and the product (2.0 g., m.p. 100–118°) was crystallized from acetone. Five recrystallizations from the same solvent gave "α-amyradiene-IV" as prismatic needles; m.p. 126–128°, $[\alpha]_D$ +150° (*c*,1.9), λ 207 mμ (ε 3800); lit.[15] m.p. 129–131°, $[\alpha]_D$ +148°. It gave a yellow color with tetranitromethane in

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(24) The fact that the norketone obtained from α-amyradiene-IV could not, in our hands, be crystallized unless the product had been equilibrated with base may be construed as evidence that an initial product undergoes change, probably epimerization, on base treatment. The most likely explanation is that the 3-methyl group epimerizes from an axial to equatorial configuration. On this evidence, the 3α- (axial) isomer (α-**8**) is favored for the structure of the parent hydrocarbon.

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chloroform solution; ν^{CS_2} 1647 and 886 cm.$^{-1}$ (vinylidene); ν^{KB} 1667, 1639, 893, 730, and 720 cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$) gave olefinic proton signals at δ 4.47, 4.76, 5.13, and 5.40.

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.5; H, 11.9.

The diene can also be isolated (less conveniently) without chromatographic treatment. α-Amyrin mesylate (150 mg.) was dissolved in pyridine (20 ml.) and heated under reflux. At intervals of 24 hr., 5-ml. fractions were withdrawn; diluted with ether; washed successively with water, 1 *N* hydrochloric acid, water, sodium hydrogen carbonate solution, and water; and dried over magnesium sulfate. The residue, obtained on evaporation, was weighed and dissolved in carbon disulfide (1 ml.); the infrared spectrum was examined. The mesylate decomposition was estimated from the 1185-cm.$^{-1}$ band and at the end of 1, 2, and 3 days was 68, 92, and *ca.* 97%, respectively, complete.

B.—A solution of α-amyrin toluenesulfonate[29] (200 mg., m.p. 128–129° dec., $[\alpha]_D$ +73°) in petroleum ether was filtered through alumina (Woelm, neutral, grade I). Elution with the same solvent gave "α-amyradiene-IV" as fine needles from ethyl acetate, m.p. and m.m.p. 126–127.5°, $[\alpha]_D$ +159° (*c* 1.1). Elution with chloroform–methanol (99:1, 200 ml.) gave α-amyrin (27 mg., m.p. and m.m.p. 183–185°, $[\alpha]_D$ +90°) as fine needles from chloroform–methanol.

Conversion of "α-Amyradiene-IV" to 1-α-Amyradiene.—Concentrated hydrochloric acid (10 ml.) was added to a mixture of "α-amyradiene-IV" (200 mg.) in chloroform (5 ml.) and acetic acid (60 ml.), and the mixture refluxed for 20 hr. The product, isolated in the usual way, was dissolved in petroleum ether (b.p. 40–60°) and chromatographed on alumina. Elution with the same solvent gave a fraction (58 mg.) which, after five recrystallizations from methanol–chloroform, gave *l*-α-amyradiene as small flat needles, m.p. 190–192°, undepressed on admixture with an authentic specimen; $[\alpha]_D$ −108° (*c* 0.8); λ 234 mμ (ε 15,000), 241 (16,200), and 250 (10,000).

Separation of Constituents of "α-Amyradiene-IV."—Thin layer chromatographic examination of "α-amyradiene-IV" on silver nitrate impregnated silica gel G revealed two dark spots of R_f values 0.57 and 0.29. Under the same conditions, α-amyradiene-II (ursa-2,12-diene) gave one spot, R_f 0.56.

A preparative separation of "α-amyradiene-IV" (75 mg.) on the same adsorbent gave the same spots, which were separated and eluted with petroleum ether. The fraction (R_f 0.57, 31 mg.) was crystallized from acetone to give ursa-2,12-diene as needles; m.p. 114–115°; $[\alpha]_D$ +135° (*c*, 1.4); ν^{KBr} 1667, 731, and 721 cm.$^{-1}$; lit.[8] m.p. 119–120°, $[\alpha]_D$ +137°. N.m.r. signals (in CCl_4) were at δ 0.78, 0.88, 0.94, 1.02, 1.06, 1.31, 5.12, and 5.32.

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 87.95; H, 11.68.

The second fraction (R_f 0.29, 26 mg.) was crystallized from acetone to give α-amyradiene-IV as heavy prisms; m.p. 155–156°; $[\alpha]_D$ +169° (*c* 0.9); ν^{KBr} 1639 and 893 cm.$^{-1}$ (vinylidene); n.m.r. signals (in CCl_4) at δ 0.76, 0.80, 0.92, 1.05, 1.12, 1.16, and 1.37 (methyl groups), 4.40, 4.67, and 5.13 (vinyl protons).

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 87.90; H, 12.20.

Acid Isomerization of α-Amyradiene-IV.—Trichloroacetic acid (50 mg.) was added to a solution of α-amyradiene-IV (50 mg.) in chloroform (2 ml.), the mixture was allowed to stand at room temperature for 1 hr., then the solvent was removed. A solution of the residue in petroleum ether was filtered through a short column (3 g.) of Florisil. The hydrocarbon fraction eluted (43 mg.) was examined by the preparative thin layer technique using silver nitrate impregnated silica gel G. Six products were apparent, that of the lowest R_f value being identified as unchanged α-amyradiene-IV (11 mg.) and that of highest R_f (0.74) identified as *l*-α-amyradiene (2 mg.) by comparison with the R_f value of an authentic specimen and ultraviolet absorption at λ 233 mμ (ε 14,900), 240 (16,150), and 249 (10,000).

Trichloroacetic acid (50 mg.) was added to a solution of ursa-2,12-diene (46 mg.) in chloroform (5 ml.) and the mixture was allowed to stand at room temperature for 5 days. Unchanged diene (40 mg.) was recovered.

Concentrated hydrochloric acid (2 drops) was added to a solution of ursa-2,12-diene (30 mg.) in chloroform (3 ml.) and the mixture was heated under reflux for 17 hr. The product, worked up in the usual way, was examined by thin layer chromatography and showed the presence only of the starting diene, which was extracted, crystallized from acetone, and had m.p. 113–116°.

Catalytic Hydrogenation of α-Amyradiene-IV.—A solution of α-amyradiene-IV (52 mg.) in acetic acid (15 ml.) and cyclohexane (15 ml.) was hydrogenated at atmospheric pressure and temperature using prereduced platinum oxide (20 mg.) as catalyst. When hydrogen uptake ceased (2 hr.), catalyst and solvent were removed and the residual oil was dissolved in benzene and chromatographed on Merck acid alumina (5 g.). Elution with benzene yielded **the product** $C_{30}H_{50}$, which crystallized from acetone as prisms, m.p. 126–127°, $[\alpha]_D$ +112° (*c* 1.2), ν^{KBr} 1667 cm.$^{-1}$ (vinylidene bands absent), n.m.r. signal at δ 5.05 (one vinyl proton).

Anal. Calcd. for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 88.24; H, 11.71.

The same product was obtained from α-amyradiene-IV by hydrogenation in ethyl acetate solution using 10% palladium on charcoal as catalyst. It differed from the hydrogenation product (m.p. 86–87°, lit. m.p. 84–85°[6] and 96–97.5°[8]) obtained from A-neoursa-3,12-diene and from urs-12-ene (m.p. 106–107°, lit. m.p. 110–112°[8] and 120–122°,[29] $[\alpha]_D$ +97°).

Oxidation of α-Amyradiene-IV.—A solution of osmium tetroxide (100 mg.) in dioxane (10 ml.) was added to a solution of α-amyradiene-IV (100 mg.) in the same solvent (10 ml.). The mixture was allowed to stand at room temperature for 16 days, saturated with hydrogen sulfide, and the precipitate was removed by filtration. The filtrate was evaporated under reduced pressure, and the residue (90 mg.) was dissolved in petroleum ether (b.p. 30–60°, 1 ml.) and chromatographed on Merck acid alumina (8 g.). Elution with petroleum ether (50 ml.) gave unchanged α-amyradiene-IV (10 mg.). Evaporation of the chloroform eluate (50 ml.) gave a crystalline solid (65 mg.), m.p. 184–185°, ν^{CHCl_3} 3521 and 988 cm.$^{-1}$ (hydroxyl), assumed to be a **diol** and not further purified.

Freshly crystallized lead tetraacetate (130 mg.) in acetic acid (5 ml.) was added to a solution of the diol (65 mg.) in acetic acid (5 ml.), and the mixture was allowed to stand at room temperature for 40 hr. It was then diluted with water and distilled. Solid sodium carbonate was added to the distillate, which was then redistilled and treated with a solution of dimedone (41 mg.) in ethanol (1 ml.). Within 5 min. a precipitate (33 mg.) settled, was collected, recrystallized from methylene chloride–ethanol, and identified as formaldehyde dimedone by m.p. 190–191° and infrared comparison with authentic specimen.[30] The residue from the initial distillation was extracted with ether, and the extract was washed with sodium bicarbonate solution and water and dried over magnesium sulfate. Evaporation of the dried extract yielded an oil (54 mg.) which was dissolved in benzene and chromatographed on Savory and Moore alumina (pH 8.5, 6 g.). Elution with benzene (50 ml.) gave an oil (45 mg.) which resisted attempts at crystallization. It was heated under reflux with 1% ethanolic potassium hydroxide solution (8 ml.) for 2 hr. On cooling, crystals separated, and recrystallization from ethanol gave the **ketone** as platelets; m.p. 152–153°; $[\alpha]_D$ +117° (*c* 0.6); ν^{KBr} 1712 cm.$^{-1}$; n.m.r. signals at δ 0.80, 0.87, 0.93, 1.05, and 1.12 (methyl groups), and 5.18 (one vinyl proton).

Anal. Calcd. for $C_{29}H_{46}O$: C, 84.81; H, 11.29. Found: C, 84.55 H, 11.50.

β-Amyrin Toluenesulfonate.—β-Amyrin (1.0 g.) and *p*-toluenesulfonyl chloride (0.5 g.) were dissolved in dry pyridine (5 ml.); the mixture was kept at room temperature for 24 hr., then poured into water, and extracted with ether. The extract was washed successively with water, dilute hydrochloric acid, sodium bicarbonate solution, and water, and dried over sodium sulfate. The residue obtained on evaporation was crystallized from petroleum ether to yield β-amyrin toluenesulfonate as needles, m.p. 126.5–127.5° dec., $[\alpha]_D$ +74° (*c* 2.0).

Anal. Calcd. for $C_{37}H_{56}O_3S$: C, 76.51; H, 9.72; S, 5.51. Found: C, 76.72; H, 9.82; S, 5.14.

β-Amyrin Methanesulfonate.—β-Amyrin (1.0 g.) and methanesulfonyl chloride (300 mg.) were dissolved in dry pyridine (3 ml.) and worked up as for the toluenesulfonate above. Crystallization from chloroform–petroleum ether or methylene chloride–methanol gave β-amyrin methanesulfonate as fine needles; m.p. 134–135° dec., $[\alpha]_D$ +82° (*c* 2.4); lit.[15] m.p. 127–128°.

(30) Formaldehyde, as its dimedone derivative, was readily isolated in low yield by similar treatment or ozonization of "α-amyradiene-IV."

Anal. Calcd. for $C_{31}H_{52}O_3S$: C, 73.76; H, 10.38; S, 6.33. Found: C, 73.45; H, 10.38; S, 6.16.

"β-Amyradiene-IV". A.—A solution of β-amyrin toluenesulfonate (530 mg.) in petroleum ether was chromatographed on alumina (Woelm, neutral, grade I). Elution with the same solvent gave a product (300 mg.) which crystallized from acetone to give "β-amyradiene-IV" as needles; m.p. 134–135°; $[\alpha]_D$ +157° (*c* 1.8); ν^{CS_2} 1650, 893 (vinylidene), and 730 cm.$^{-1}$.

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.00; H, 12.00.

Elution with chloroform gave β-amyrin (204 mg.), crystallized from chloroform–methanol as needles, m.p. and m.m.p. 194–195°, $[\alpha]_D$ +95°.

B.—In a similar experiment, β-amyrin methanesulfonate (300 mg.) gave 249 mg. of crude "β-amyradiene-IV" and 20 mg. of β-amyrin.

C.—In an experiment using Woelm basic alumina, the methanesulfonate (500 mg.) gave 300 mg. of "β-amyradiene-IV."

D.—A solution of β-amyrin methanesulfonate (650 mg.) in dry pyridine (7 ml.) was heated under reflux for 7 days and worked up as in the corresponding preparation (A) of "α-amyradiene-IV" to give "β-amyradiene-IV" as needles, m.p. 137–138°, $[\alpha]_D$ +152°, after three recrystallizations from acetone.

Separation of Constituents of "β-Amyradiene-IV."—"β-Amyradiene-IV" (90 mg.) was subjected to thin layer chromatography under the same conditions as applied to the separation of "α-amyradiene-IV." Again, two principal spots were detected. The fraction (R_f 0.37, 70 mg.) was crystallized from acetone as needles to give oleana-2,12-diene; m.p. 145–147°; $[\alpha]_D$ +136° (*c* 0.6); ν^{KBr} 1667, 730, and 725 cm.$^{-1}$; lit.[8] m.p. 150–153°, $[\alpha]_D$ +140°.

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.10; H, 11.65.

The second fraction (R_f 0.15, 13 mg.) was crystallized from acetone to give β-amyradiene-IV as prismatic needles; m.p. 167–169°; $[\alpha]_D$ +167° (*c* 0.4); ν^{KBr} 1656 and 893 cm.$^{-1}$; n.m.r. signals (in CCl_4) at δ 5.17, 4.69, and 4.41, each with integrated intensity of one proton.

Anal. Calcd. for $C_{30}H_{48}$: C, 88.16; H, 11.84. Found: C, 88.36; H, 11.67.

Recrystallization of "β-amyradiene-IV" six times from acetone or three times from chloroform–methanol gave oleana-2,12-diene as needles, m.p. and m.m.p. 154–155°, $[\alpha]_D$ +145° (*c* 1.8).

Solvent Effects in Quantitative Structure–Reactivity Correlations of Esters

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The rates of alkaline hydrolysis of eight ethyl esters have been correlated by the extended Taft linear free-energy relationship in both 85% aqueous ethanol and 85% aqueous dimethyl sulfoxide. The solvent dependence of the polar, steric, and hyperconjugative resonance reaction constants are discussed in terms of differences in transition-state solvation mechanisms. An increased importance of steric interference with solvation of the activated complex in aqueous dimethyl sulfoxide relative to aqueous ethanol is suggested by the data.

The dependence of substituent effects upon reaction medium has attracted increasing attention over the past few years. Thus, Grunwald and Berkowitz[1] found the variation with solvent of the reaction constant ρ for the dissociation of *meta*- and *para*-substituted benzoic acids is given quantitatively as a linear function of the activity function *Y*. Fuchs and Nisbett[2] reported that ρ for the reaction of *para*-substituted α-chlorotoluenes with thiosulfate anion varies linearly with $1/D$ in a variety of organic solvents.

In a related study Ritchie and Lewis[3] demonstrated that the solvent dependence of substituent effects on the acidities of a series of 4-substituted bicyclo[2,2,2]-octane-1-carboxylic acids is attributed to factors other than direct interaction of substituent and reaction site.

Most recently Taft and co-workers[4] observed the effect of four specific solvent–substituent interactions based on extensive measurements of fluorine nuclear magnetic resonance shielding in the *meta*-substituted fluorobenzenes. Of particular interest to the present study, their data reveal a solvent interaction between dimethyl sulfoxide and ester functions based on solvent polarity but no definite evidence for a complex between an ester function and dimethyl sulfoxide.

Previously, it was reported[5] that the rate of alkaline hydrolysis of ethyl benzoate exhibits a significantly different dependency upon solvent composition when aqueous dimethyl sulfoxide is substituted for aqueous ethanol. The presence of microscopic solvent–solute interactions were proposed as an explanation for these observations.[6]

In order to further delineate the specific solvation interactions, it was decided to study solvent effects on a quantitative structure–reactivity relationship. Such an investigation permits a more discriminating assessment of the medium effects by measuring the susceptibility of the reaction to polar, resonance, and steric substituent effects.

For a series of esters, RCO_2R', where the R′ group is fixed while the R group is varied, the saponification rate constants, *k*, are defined by the following (eq. 1[7])

$$\log k = \log k_0 + \rho^*\sigma^* + \delta E_s \qquad (1)$$

where k_0 is the regression value for the saponification constant of CH_3CO_2R', ρ^* is the polar reaction constant,[8a] σ^* is the polar substituent constant[8b] for the R group, δ is the steric reaction constant,[8c] and E_s is the steric substituent constant[8c] for the R group.

Hancock[9] modified the steric substituent constant by quantitative separation of hyperconjugation effects according to the expression shown in eq. 2 following

$$E_s^c = E_s - h(n - 3) \qquad (2)$$

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