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CHEMICAL EXAMINATION OF DIOSPYROS SPECIES-PART V: A NOVEL AROMATISATION OF RING B AND OTHER REACTIONS OF BAUERENOL

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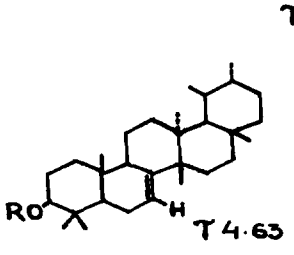
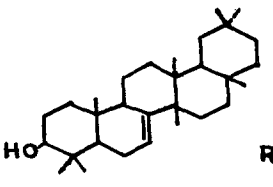
The structure of bauerenol (I,R=H), proposed by Lahey and Leeding[1], received full support from a study of its mass spectrum by Djerassi[2]; yet the chemistry of bauerenol is incomplete. Recently, bauerenol (I,R=H) was also noticed along with the isomeric multiflorenol (II) in the bark of Gelonium multiflorum[3] and in the leaves of Diospyros melanoxylon[4] and Diospyros sylvatica[5]. This short communication now describes certain reactions of bauerenol (I,R=H) which lead to a hitherto unknown aromatisation of ring B.



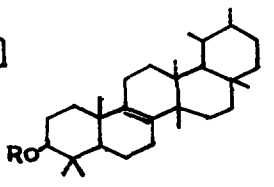
I

τ-Methyls
9.27
9.15
9.07
9.03
8.92

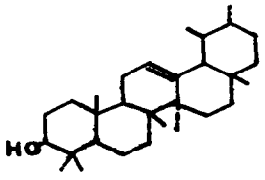


II

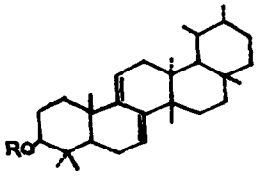
τ-Methyls
9.18
9.12
9.04
8.98
8,92



III



IV

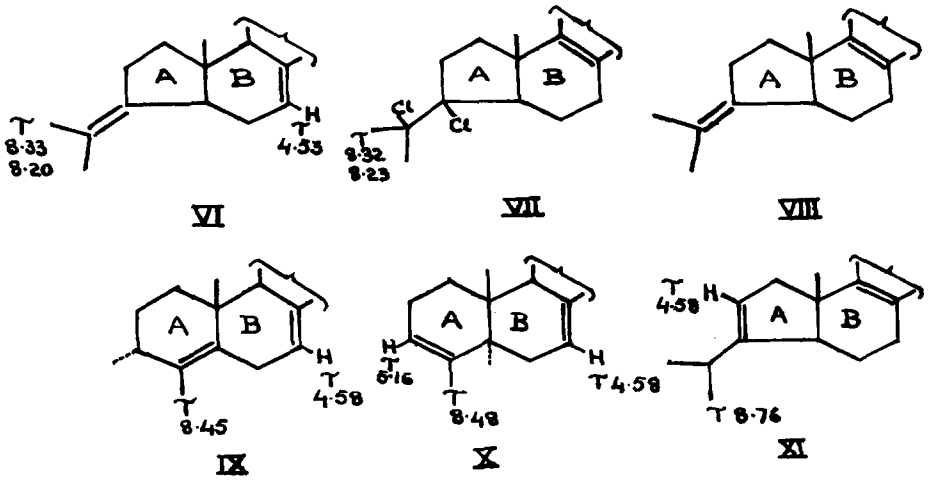


V

In several respects, bauerenol (I,R=H) behaved peculiarly. The protonic reagent, HOAc+H_2SO_4, had varying influence on bauerenyl acetate (I,R=Ac) depending upon concentration, temperature and time. When it was just warmed to dissolve in acetic acid containing a few drops of H_2SO_4 and kept at room temperature for 15 mts, isobauerenyl acetate, (III,R=Ac) separated out as colourless needles, m.p. 220-22°; $(\alpha)_D^{30}$+ 40°. On the other hand, acetic acid containing 2% H_2SO_4 converted bauerenyl acetate into α-amyrin (IV) when kept at 30° for 2 hrs. But, when it was boiled with 7% H_2SO_4 -AcOH for 4 hrs., an oily product was obtained which showed no -OH or -OAc frequencies in its I.R. spectrum. When the same reaction was carried out with baueradienyl acetate (V,R=Ac), a colourless crystalline solid was secured , m.p. 144-46°; $(\alpha)_D^{30}$+ 10° which again showed no absorption for a -OH or -OAc. This compound analysed for $C_{30}H_{46}$ and did not absorb between 210 and 300 mμ in U.V. This reagent, therefore, caused loss of an acetic acid molecule from both bauerenyl acetate (I,R=Ac) and its diene (V,R=Ac)

Further, the action of PCl_5-petrol and $POCl_3$-pyridine on bauerenol (I,R=H) and isobauerenol (III,R=H) also gave interesting results. With PCl_5, bauerenol (I,R=H) suffered normal retropinacolinic rearrangement to give VI (m.p. 178-80°; $(\alpha)_D^{30}$ −13°) while isobauerenol (III,R=H) gave rise to a dichloro adduct[6] VII (m.p. 170-72°; $(\alpha)_D^{30}$ +35°). Zinc and acetic acid[7] removed the two chlorines from VII giving rise to an oily product whose I.R. was consistant with the structure VIII.

$POCl_3$-pyridine, however, differed in its action over bauerenol (I,R=H) and isobauerenol (III,R=H). The former (I,R=H) gave rise to two products, IX (m.p. 152-54°; $(\alpha)_D^{30}$ — 50°) and X(m.p. 122-24°; $(\alpha)_D^{30}$—15°) which differed considerably in their I.R. spectra. Further, solvolysis (AcOH+NaOAc) of bauerenyl p-toluene sulphonate (I,R=Ts) caused facile transformation to a compound identical in every respect (m.m.p. & I.R.) with IX. Isobauerenol (III,R=H), on the other hand, gave rise to an oily product along with a minor quantity of a colourless crystalline solid XI (m.p. 158-60°; $(\alpha)_D^{30}$+ 115°) when treated with Py-$POCl_3$;



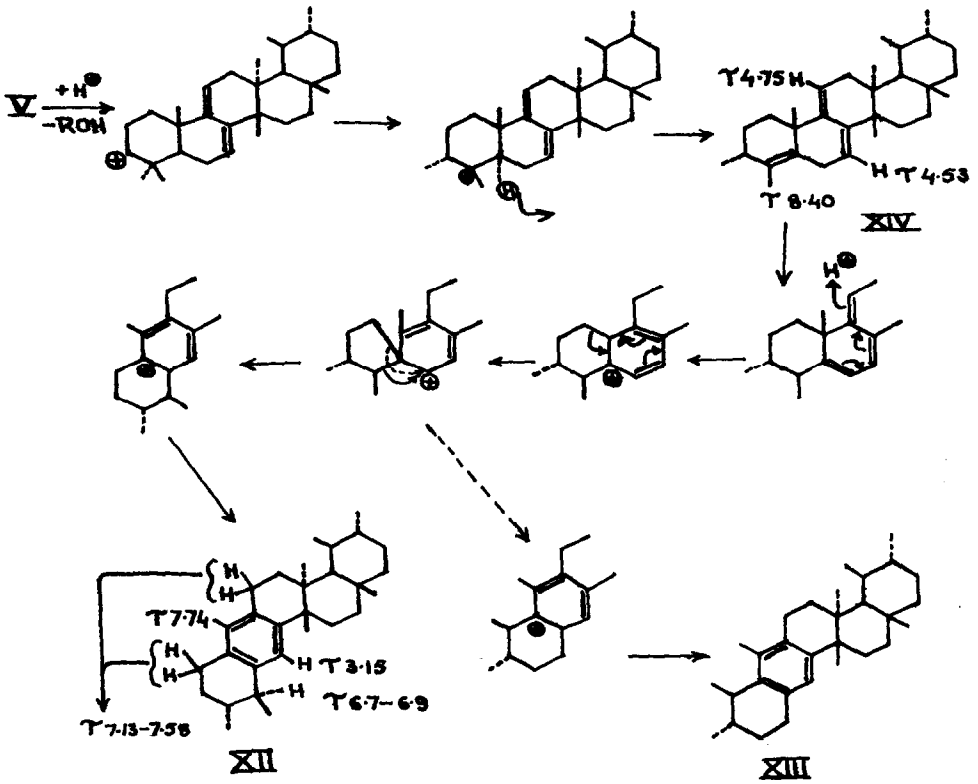
At this stage, the structures of various rearranged products (VI, VII, IX, X and XI) were studied with the help of their N.M.R. spectra. Incidentally, the N.M.R. spectra of bauerenol (I,R=H) and isobauerenol (III,R=H) have also been put forward for the first time. The olefinic 7-H of bauerenol (I,R=H) gave a triplet (J=2 cps) centered at τ4.63 which was absent in isobauerenol (III,R=H). PCl_5 dehydration product (VI) of bauerenol (I,R=H) had a gem-dimethyl group at τ8.20 and 8.33 (singlets) suggesting a powerful paramagnetic shift presumably due to a Δ^3 double bond. A similar shift (τ8.23, 8.32) was also noticed in the gem-dimethyl group of PCl_5 dehydration product (VII) of isobauerenol (III,R=H). But analysis of VII indicated that it should be an adduct with two Cl atoms at 3,4-positions, the 4-Cl causing the paramagnetic shift of the gem-dimethyls.

The $POCl_3$-pyridine dehydration of bauerenol (I,R=H) caused the formation of two products IX and X whose N.M.R. spectra indicated a methyl shift. In IX, the signal at τ8.45 integrates for one methyl and must be due to the paramagnetic shift of Δ^4 double bond. In X, an allylic system comprising one methyl (τ8.48) and a single proton (τ5.16 triplet) is easily discernable and this can be reasonably located in ring A. In addition, 7-H is noticeable at τ4.58 in both IX and X as in bauerenol(I,R=H).

A similar N.M.R. study of $POCl_3$-pyridine dehydration product (XI) of isobauerenol (III,R=H) showed one olefinic proton at τ4.58 and a gem-dimethyl group at τ8.76 (singlet). The methyl signals indicated no methyl shift. Obviously, the olefinic system does not influence the gem-dimethyl group. Since it could be in ring A only, the obvious choice is 2=3 and the proton is located at 2, the alternate position 5=6 being too remote to be considered. It may be pointed out that the major product in this reaction was an oil and its I.R. spectrum indicated only a tetrasubstituted double bond.

The N.M.R. spectrum of the 7% H_2SO_4-AcOH reaction product of baueradienyl acetate (V,R=Ac) was very peculiar. It showed evidence for one aromatic methyl at τ7.74 and one uncoupled aromatic hydrogen at τ3.15. Further there was a single proton at τ6.7-6.9 (multiplet) indicating a benzal hydrogen and at τ7.13-7.58 (broad), a total of four protons are indicated for two benzyl 'CH_2' groups. These signals clearly show that baueradienyl acetate (V,R=Ac) was undergoing an unusual aromatisation not hitherto noticed in triterpences. Rearrangement leading to aromatisation of ring B with protonic reagents was noticed with 9-dehydroergosterol and 7-dehydrocholesterol [8,9] which was named anthrasteroid rearrangement. This name is inappropriate and could not be adopted in the present case. However, a similar mechanism [10] (Chart A) appears to be feasible during the aromatisation of baueradienyl acetate (V,R=Ac) which leads to two feasible structures XII and XIII for the aromatised product. It had not been possible from the N.M.R. data to clearly allocate structure XII or XIII for the aromatised product. However, the single sharp peak at τ7.74 would show that the aromatic methyl was not coupling with a methyl or a proton of ring A and this was feasible in XII and not in XIII.

C H A R T-A



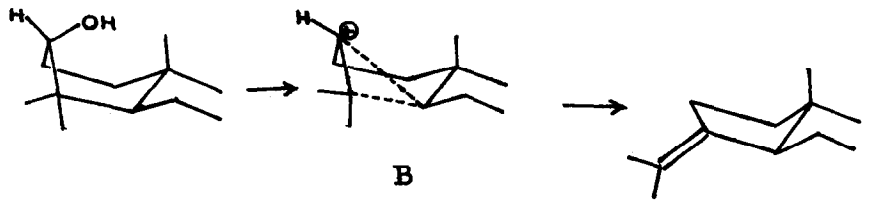
τ-Methyls:

9.42, 9.30, 9.22, 9.10 to 8.87.

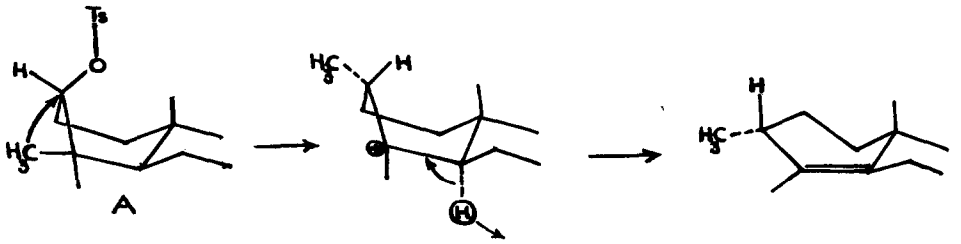
A study of chart A suggests that a compound (XIV) similar to IX should have been an intermediate. An attempt is therefore made to prepare a compound with structure XIV from baueradienol (V,R=H). The solvolysis of bauerenol p-toluene sulphonate has already been shown to give rise to IX. Now a similar reaction was performed with baueradienyl p-toluene sulphonate (V,R=Ts) whereby a triene was secured which had U.V. absorption at 232, 239 and 247 mμ confirming a heteroannular diene system and no homoannular diene system (peak absent at 280 mμ). Structure XIV, therefore, correctly represents this product. This triene (m.p. 138-40°;

($[\alpha]_D^{30}$ — 150°) was also formed when baueradienol (V,R=H) was treated with pyridine-$POCl_3$, and cyclised readily as predicted above, on refluxing with 7% H_2SO_4-AcOH to give XII in 90% yield. It is significant to record here that PCl_5-petrol did not cause any retropinacolic rearrangement of baueradienol (V,R=H); the product was identical (m.m.p., I.R. and N.M.R) with the triene XIV, whose N.M.R showed a single methyl shift at τ8.40 and one proton at τ4.53 (7-H, triplet) and another centered at τ4.75 (11-H, broad multiplet).

The behaviour of bauerenol (I,R=H) towards PCl_5-petrol and pyridine-$POCl_3$ is not easy to explain, for these two reagents are well known to cause retropinacolinic rearrangement in 3-β-hydroxy triterpenses. The methyl shifts caused by the latter reagent (see IX and X) may be better explained on the basis that ring A of bauerenol might have the boat conformation in which the 4-gem dimethyls are comparatively free from the 1:3 axial interactions from 10-CH_3 and so can take part in the normal (backward) 1:2-methyl shift, obviously through the intermediate A. PCl_5-petrol on the other hand leads to the formation of the intermediate carbonium ion (B) which favour rapid retropinacolinic rearrangement. This is readily noticeable if conformations of ring A are studied with the aid of Dreiding models.



B



Chair conformation of ring A in 3-β-hydroxy triterpenes will cause retropinacolinic rearrangment which is aided significantly by the repulsion between 4-gem dimethyl and 10-methyl groups[11]. The presence of a Δ^5 double bond in ring B[12] or $\Delta^{5(10)}$ double bond[13] in ring A can alter the course of rearrangement; but the presence of Δ^7 bond does not seem to exert any influence in bauerenol (I,R=H). Our studies of the action of PCl_5-petrol and pyridine-$POCl_3$ on multiflorenol (II) amply justify this conclusion. Both reagents caused retropinacolinic rearrangement, strongly suggesting that ring A in multiflorenol (II) must possess chair conformation, different from that of bauerenol (I,R=H). Again, in contrast to that of bauerenol (I,R=H), isobauerenol (III,R=H) suffers retropinacolinic rearrangement with PCl_5-petrol or pyridine-$POCl_3$ (see VII, VIII & XI) strongly favouring a chair structure for ring A.

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