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THE AROMATISATION REACTION OF RING B OF $\Delta^{7,9(11)}$-TRITERPENOIDS

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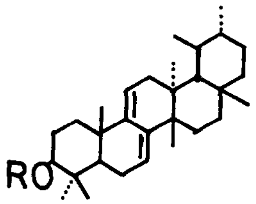
A novel aromatisation reaction of ring B, similar to anthrasteroid rearrangement, of bauera-7,9(11)-dienyl acetate (I, R : Ac) by acetic acid-sulfuric acid to form a hydrocarbon (II) was reported by Row and Rao.(1) In the course of the application of the reaction to 7,9(11)-dienes (III - VI) of tirucallane, lanostane, fernane, and arborane series to compare the properties of diastereomeric pairs of hydrocarbons thus formed, we learned that the structures of the hydrocarbons obtained by us should be expressed by the structures (VII - X) and the reexamination of the reaction of I (R : Ac) became necessary.

By refluxing I (R : Ac)(2) with 7 % H_2SO_4-HOAc for 2 hrs. an aromatic hydrocarbon, m.p. 145°, $[\alpha]_D$ + 17.8°, M^+ 406 m/e, $\lambda_{max}^{cyclohexane}$ mμ (log ε) : 262 (2.48), 270.5 (2.60), 279.5 (2.51), ν_{max}^{KBr} cm^{-1}: 1608, 1589, 1470, 810, 789, was obtained in a good yield and was proved to be identical with the compound (II) obtained by Row and Rao.(3) The same compound was also obtained from bauera-7,9(11)-dien-3β-ol (I, R : H) and from 3β-methoxybauera-7,9(11)-diene (I, R : Me) under the same reaction condition. However the presence of M^+ - 43 peak (m/e 363) in the mass spectrum suggested the presence of isopropyl group in the molecule. Decoupling experiments revealed that the aromatic methyl group (τ 7.76, 3H, w 1/2 ca. 4 cps) and the ring proton (τ 3.24, 1H, w 1/2 ca. 4 cps) are in neighboring positions (the irradiation of the former signal sharpens the latter and increases the area (13.2 %)) and that none of the five benzylic protons (τ 7.40 (m, 4H), 6.85 (m, 1H)) is coupled with the secondary methyl groups. These facts are not tenable for the structure (II) but suggest the structure (XI).



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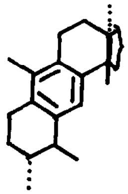

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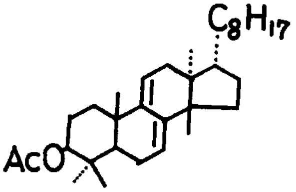

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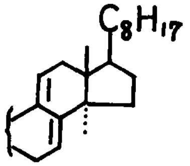

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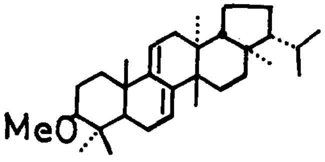

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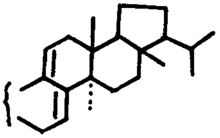

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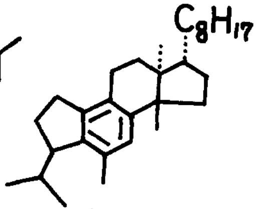

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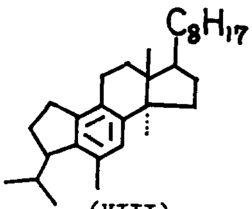

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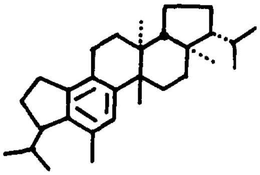

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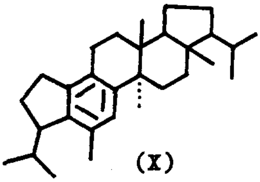

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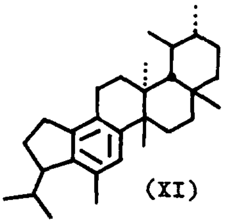

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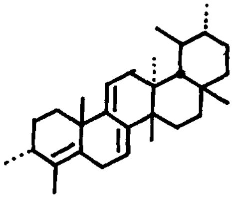

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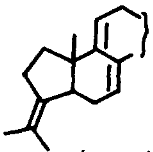

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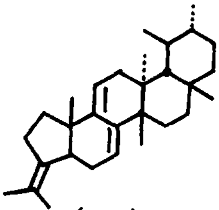

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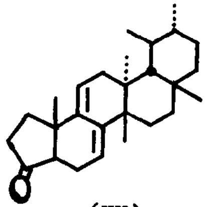
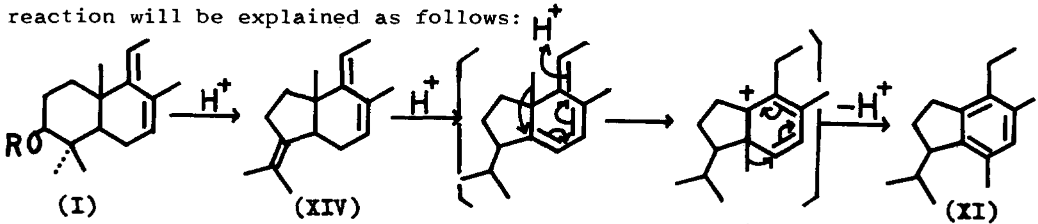


(XV)

Table 1

	m.p.	$[\alpha]_D$	UV $\lambda_{max}^{cyclohexane}$	NMR	τ ($CDCl_3$)
		($CHCl_3$)	(mμ)	arom. Me	ring H
VII	141.5-142.5°	-20°	261.5, 270, 279.5	7.72	3.28
VIII	liquid	+44.3°	262, 269.5, 279	7.71	3.33
IX	157-159°	-16°	262, 270, 279.5	7.72	3.17
X	181.5-182.5°	+48.5°	262, 270, 279.5	7.71	3.19

Row and Rao(1) claimed that the dehydration with PCl_5 or $POCl_3$ of bauera-7,9(11)-dien-3β-ol (I, R : H) gave a triene (XII), the acid treatment of which gave the aromatic hydrocarbon (II). However, in the case of dihyroagnosterol (IV), the formation of a normal retropinacolin rearrangement product (XIII) and 2,7,9(11)-triene respectively by the treatment with PCl_5 and $POCl_3$ was reported.(4) Treatment of I (R : H) with PCl_5 in petr. ether at 0° or at a room temperature gave a mixture of products, from which a hydrocarbon (XIV), m.p. 130-132°, $[\alpha]_D$ - 167.5°, λ_{max}^{hexane} mμ (log ε) : 232.5 (4.11), 239.5 (4.13), 247.5 (3.91), τ8.30, 8.37 (each 3H, allyl methyls), 4.6, 4.8 (each 1H, vinyl protons), was isolated as the major product. In order to confirm the structure of the product (XIV), it was oxidized with OsO_4 in ether and the diol thus formed, m.p. 177-178°, $[\alpha]_D$ - 143°, ν_{max}^{KBr} 3400 cm^{-1}, was further oxidized with $Pb(OAc)_4$ in AcOH-benzene to afford a five-membered ketone (XV), m.p. 172-174°, $[\alpha]_D$ - 236°, λ_{max}^{hexane} mμ (log ε) : 232 (4.12), 239 (4.15), 247.5 (3.92), $\nu_{max}^{CCl_4}$ cm^{-1}: 1741, CD, negative Cotton effect (θ_{296} Δε - 3.76, θ_{307} Δε - 3.75), and acetone, which was identified as the 2,4-dinitrophenylhydrazone. Thus the structure of the triene was established as (XIV). Treatment of (XIV) with 7 % H_2SO_4-HOAc under reflux for 2 - 4 hrs. gave the aromatic hydrocarbon, which was identified with the product (XI) directly obtained from I. These facts clearly demonstrate the structure (XI) and the course of the novel aromatisation reaction will be explained as follows:



The acid treatment of tirucalla-7,9(11)-dienyl acetate(5) (III), dihyroagnosteryl acetate(6) (IV), 3β-methoxyferna-7,9(11)-diene(7) (V), and 3β-methoxyarbora-7,9(11)-diene(7) (VI) afforded the same type of aromatic hydrocarbons (VII, VIII, IX, X). The physical data suggesting the structures of these compounds are shown in Table 1.

All these aromatic hydrocarbons show the peak (M^+ - 43). The ORD curves of the aromatic hydrocarbons are shown in Fig. 1. The compounds having 13α, 14β-methyls (VII, IX, XI) show the same negative back plain curves, while those with 13β,14α-methyls (VIII, X) show the same type of positive curves, which coincide with those reported in the case of estrogenic steroids and the related compounds.(8) All these compounds show nearly the same multiple Cotton effect curves at 260 - 290 mμ irrespectively with C_{14}-configurations and the sign suggests that 1S-configurations in indan system,(9) supporting the β-configuration of the isopropyl groups in the hydrocarbons (VII - XI).

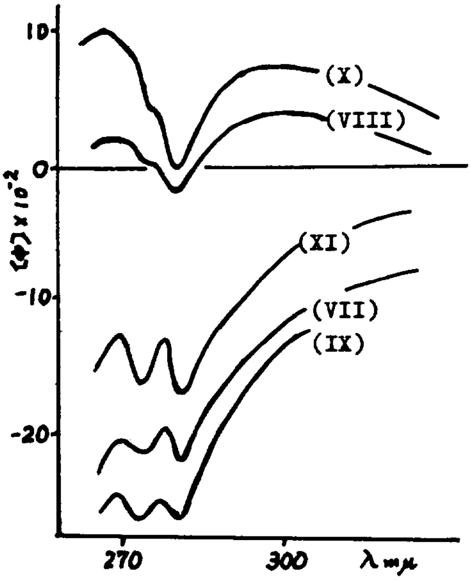


Fig. 1 ORD curves of the aromatic hydrocarbons (VII - XI)

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(2) In this study bauerenol obtained from *Ardisia sieboldii Miquel*. (H. Ogawa and S. Natori, *Chem. Pharm. Bull.*, **16**, 1709 (1968)) was used for the starting material. The identity of bauerenol and 'ilexol' and some reaction of bauerenol to reconfirm the position of the double bond at 7-position will be reported in a separate paper (M. Fukuoka and S. Natori: *Chem. Pharm. Bull.* (Japan), to be published).

(3) The authors thank Professor L. R. Row, Andhra University, India, for his generous gift of the specimen.

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