

Lantadene A. The Active Principle of *Lantana camara* L. Part IV.—Dehydrogenation of Lantadene A and Lantadene B.

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DEHYDROGENATION results of Lantadene A suggest an immediate relationship of this compound to the triterpenoid sapogenins, a group of compounds which was first recognized by Ruzicka and his co-workers (1932).

On dehydrogenation of Lantadene A with selenium, a $C_{13}H_{14}$ hydrocarbon with B.P. $130^{\circ}C./10$ mm. Hg was obtained as the main degradation product. It forms a picrate with M.P. $130^{\circ}C.$ and a styphnate with M.P. $156^{\circ}C.$ These properties correspond with those of sapotalene (1, 2, 7-trimethylnaphthalene).

Oxidation of the hydrocarbon with potassium ferricyanide according to the original method of Weissgerber and Kruber (1919) as modified by Ruzicka *et al.* (1926) for the oxidation of sapotalene, yields an acid product which on methylation with diazomethane gives a crystalline product with M.P. 152° - $154^{\circ}C.$ C and H values of this compound correspond with the formula $C_{16}H_{14}O_6$. The trimethylester $C_{16}H_{14}O_6$ obtained by Ruzicka by oxidation of sapotalene has M.P. 153° - $154^{\circ}C.$

The $C_{13}H_{14}$ hydrocarbon obtained from Lantadene A was finally identified as sapotalene by mixed melting point determinations of the picrate and styphnate with synthetic sapotalene picrate and styphnate.

From the dehydrogenation reaction mixture a $C_{17}H_{16}$ hydrocarbon along with a compound $C_{17}H_{16}O$ (possibly a phenanthrol) was isolated.

In 1934 Ruzicka *et al.* obtained a $C_{17}H_{16}$ hydrocarbon by selenium dehydrogenation of hederagenin, $C_{30}H_{48}O_4$. This hydrocarbon was proved to be 1, 2, 6-trimethylphenanthrene.

Table 1 summarises the melting points of the few known trimethylphenanthrenes out of the 60 possible isomers.

The $C_{17}H_{16}$ hydrocarbon from Lantadene A was identified as 1, 2, 6-trimethylphenanthrene by comparison with a sample of synthetic hydrocarbon.

TABLE I.

Trimethyl Phenanthrene.	M.P. ° C.	Picrate M.P. ° C.	Styphnate M.P. ° C.	Quinone M.P. ° C.	Quinoxaline M.P. ° C.	Reference.
1.2.7.....	120-1	148-9	169-170	209-210	184-5	Haworth, J. C. S. (1932), 2248.
1.3.7.....	68-9	163-4	160-1	174-5	201-2	Haworth, J. C. S. (1932), 2248.
1.6.7.....	123-4	165-6	111-2	221-2	189-190	Haworth, J. C. S. (1932), 2248.
1.2.8.....	144-5	163	—	196-7	130-1	Haworth, J. C. S. (1932), 2720. Ruzicka, H. C. A. (1940), 124-131.
1.4.7.....	72-3	141-2	129-130	170-1	140-1	Haworth, J. C. S. (1932), 1784.
2.6.9.....	78	169-170	—	—	—	Ritter, J. A. C. S. (1940), 62, 1508-9.
1.2.3.....	64-5	187-8	—	—	—	Fieser, J. A. C. S. (1941), 63, 782-8.
1.2.6.....	128-9	167-8	174-5	207-8	182-3	Ruzicka, H. C. A. (1934), 17, 447.
C ₁₇ H ₁₆	131-2	168-9	178-180	—	—	From Lantadene A.

Similarly, sapotalene and 1, 2, 6-trimethylphenanthrene could be obtained by dehydrogenation of both Lantadene B and the resin breakdown product of Lantadene A, viz C₁₇H₂₆O₃, which reveals a close similarity of Lantadene A and Lantadene B.

EXPERIMENTAL.

A. Dehydrogenation of Lantadene A.

A dehydrogenation apparatus as described by Ruzicka *et al.* (1932) was used.

Firstly the optimum-dehydrogenation temperature was determined by leading the generated gases through a copper tube into a flame. The presence of selenium-hydride was easily determined by means of the blue flame with which it burned, while giving off white fumes of selenium-oxide. The temperature at which a steady stream of selenium-hydride was developed was considered as a suitable temperature for conducting the dehydrogenation.

25 gm. Lantadene A, thoroughly dried in an exsiccator were mixed with 60 gm. dry red amorphous selenium. The mixture was then slowly heated by means of a KNO₃/NaNO₃ bath. It first melted at about 300° C. while gas bubbles escaped. A colourless liquid now began to distil. This liquid was previously obtained by the dry-distillation of Lantadene A and was identified as a lactone, C₆H₈O₂. Lantadene A, therefore, firstly decomposed above its melting point into the lactone and the resin. The bath temperature was slowly increased when selenium-hydride began to come off at 320° C. The bath temperature was regulated at 320° C. and slowly raised to 360° C. as dehydrogenation proceeded. The mixture was heated for 72 hours in all.

After cooling, the reaction mixture was dissolved out with chloroform. The chloroform was evaporated and the residue extracted with ether. The ether was evaporated leaving 8 gm. of a brown, fluorescent oil. The product was fractionally distilled.

Fraction I.

Bath temperature up to 150° C./5 mm. Hg: Yellow liquid began to distil.

Fraction II.

Bath temperature 150-200° C./5 mm. Hg: 4 gm. of a yellow liquid distilled.

Fraction III.

Bath temperature 200-300° C./5 mm. Hg: A thick brown liquid which crystallised spontaneously, distilled.

Higher distillation fractions could not be obtained.

B. $C_{13}H_{14}$ —*Hydrocarbon.*

(1) *Properties.*

The distillate from fraction II was distilled over sodium metal when a colourless liquid with almost no smell was obtained. The liquid had a high refractive index and boiled at 130° C./10 mm. Hg.

(2) *Analysis.*

(i)	3.665	mgm. substance:	12.173	mgm. CO_2 :	2.557	mgm. H_2O .
(ii)	2.808	mgm. substance:	9.327	mgm. CO_2 :	2.093	mgm. H_2O .
(iii)	4.342	mgm. substance:	14.454	mgm. CO_2 :	3.055	mgm. H_2O .
Calculated $C_{13}H_{14}$: C=91.73%; H=8.29%						
Found	(i)	C=90.59%; H=7.81%				
	(ii)	C=90.61%; H=8.34%				
	(iii)	C=90.81%; H=7.87%				

(3) *Molecular Weight.*

0.619 mgm. in 5.289 mgm. Camphor; $\Delta = 27.5^\circ$

Found: 168.6.

Calculated $C_{13}H_{14}$: 170.

(4) *Picrate.*

A few drops of the liquid were dissolved in a few ml. alcohol and treated with a hot alcoholic solution of picric acid when an orange-red picrate crystallised on cooling. After recrystallisation it melted at 130-132° C.

Analysis.

3.577 mgm. substance: 7.275 mgm. CO_2 : 1.435 mgm. H_2O .

1.943 mgm. substance: 0.222 ml. N_2 at 23.5° C. and 624.5 mm. Hg.

Calculated $C_{13}H_{14} \cdot C_6H_3N_3O_7$: C=57.14%; H=4.29%; N=10.52%

Found C=55.47%; H=4.49%; N=10.81%

(5) *Styphnate*.

The styphnate was prepared similarly to the picrate, recrystallised from 96 per cent. alcohol, and melted at 156° C.

(6) *Oxidation of C₁₃H₁₄*.

2.15 gm. of the C₁₃H₁₄—hydrocarbon, distilled over sodium, was oxidised with potassium ferricyanide and potassium-hydroxide at a constant temperature of 60° C.

After oxidation the mixture was made acid with hydrochloric acid and shaken out with ether. The ether was evaporated leaving a residue weighing 0.22 gm. This product was dissolved in 100 ml. dry ether and treated with excess of an ethereal solution of diazomethane and left in a refrigerator for four days. The mixture was then left at room temperature for two more days and finally evaporated leaving an oily residue. This was taken up in methanol from which it crystallised in colourless plates with M.P. 152-154° C.

Analysis.

3.580 mgm. substance: 8.278 mgm. CO₂: 1.465 mgm. H₂O.

Calculated C₁₆H₁₄ O₆: C=63.60%; H=4.60%

Found: C=63.08%; H=4.58%

(7) *Mixed Melting Point Determinations and Identification.*

Small samples of synthetic 1.2.7—trimethylnaphthalene picrate and styphnate were kindly supplied by Dr. Kon of the Chester Beatty Research Institute, London. After recrystallisation they melted at 132° C. and 156° C., respectively.

When a mixed melting point determination of the C₁₃H₁₄—picrate from Lantadene A and synthetic sapotalene—picrate was made, no depression in melting point was observed. Similarly no depression of the melting point was obtained when the two styphnates were mixed and melted.

C. C₁₇H₁₆—*Hydrocarbon.*

The hydrocarbon, obtained from fraction III, was recrystallised from alcohol when it was obtained in colourless prisms with M.P. 131-132° C.

(1) *Analysis.*

3.618 mgm. substance: 12.201 mgm. CO₂: 2.217 mgm. H₂O.

1.744 mgm. substance: 5.912 mgm. CO₂: 1.144 mgm. H₂O.

Calculated C₁₇H₁₆: C=92.73%; H=7.27%

Found: C=92.45%; H=7.34%

(2) *Molecular Weight.*

0.560 mgm. in 6.199 mgm. camphor. Δ = 16.8°

Calculated C₁₇H₁₆: 220.

Found: 212.9.

(3) *Picrate*.

Recrystallised from alcohol the picrate was obtained in orange-red needles with melting point 168-169° C.

(4) *Styphnate*.

The styphnate recrystallised from alcohol has M.P. 178-180° C.

(5) *Identification of the C₁₇H₁₆—Hydrocarbon*.

A sample of synthetic 1, 2, 6—trimethylphenanthrene was kindly supplied by Dr. Ruzicka of Zurich. It was in the form of colourless prisms with a M.P. of 132° C.

Equal amounts of the synthetic hydrocarbon and the C₁₇H₁₆—hydrocarbon (M.P. 131-132° C.) were carefully mixed and melted. The mixture melted at 132° C. The melt was allowed to cool when it crystallised again. On melting the crystalline mixture, the melting point remained unchanged at 132° C.

D. C₁₇H₁₆O.

From the distillation—residue a yellow amorphous product with M.P. 130° C. was obtained.

Analysis.

3.662 mgm. substance: 11.662 mgm. CO₂: 2.098 mgm. H₂O.

Calculated C₁₇H₁₆O: C=86.40%; H=6.82%

Found: C=86.85%; H=6.41%

E. *Dehydrogenation of Lantadene A—Resin*.

17.4 gm. resin obtained from the dry distillation of Lantadene A were powdered and thoroughly mixed with 30 gm. red amorphous selenium and the mixture heated at 330-360° C. for 35 hours. The reaction product was fractionally distilled yielding:—

Fraction I.

Bath temperature 150-200° C./5 mm. Hg: 3.5 ml. liquid.

Picrate of liquid: M.P. 130° C. Mixed melting point with sapotalene-picrate: No depression.

Fraction II.

Bath temperature 200-300° C./5 mm. Hg: A thick yellow-orange liquid distilled. Prismatic crystals formed in the distillate. The crystals were separated and crystallised from alcohol when it melted at 132° C.

Mixed with 1, 2, 6—trimethylphenanthrene no depression of melting point was found.

F. *Dehydrogenation of Lantadene B.*

15 gm. Lantadene B were mixed with 40 gm. selenium and heated at 340-350° C. for 35 hours. The reaction mixture was extracted with ether, the ether evaporated and the residue fractionally distilled.

Fraction I.

Bath temperature 150-200° C./5 mm. Hg: 3 ml. yellow liquid distilled.

Picrate M.P. 130° C.

Mixed with sapotalene-picrate no depression was obtained.

Fraction II.

Bath temperature 200-300° C./5 mm. Hg: A thick brown liquid distilled. Colourless crystals separated in the distillate.

The crystals were separated and crystallised from alcohol when they melted at 132° C. Mixed with 1, 2, 6 trimethylphenanthrene no depression of melting point was observed.

SUMMARY.

1. Dehydrogenation of Lantadene A with selenium yielded sapotalene and 1, 2, 6-trimethylphenanthrene, along with a $C_{17}H_{16}O$ compound.
2. Dehydrogenation of Lantadene A-resin and Lantadene B similarly yielded sapotalene and 1, 2, 6-trimethylphenanthrene.

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