

THE CONVERSION OF FRIEDELIN INTO METHYL TETRANORSHIONANOATE

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SHIONONE is one of the constituents of Aster tataricus L. The structure 1 has been proposed<sup>1)</sup> for shionone on the basis of chemical degradations, as well as by means of biogenetic considerations. In the preceding communication<sup>2)</sup>, the nature of rings C and D has been clarified, and evidence leading to the structure 1 for shionone has been presented.

We now describe the conversion of friedelin (2) into methyl tetranorshionanoate (13).

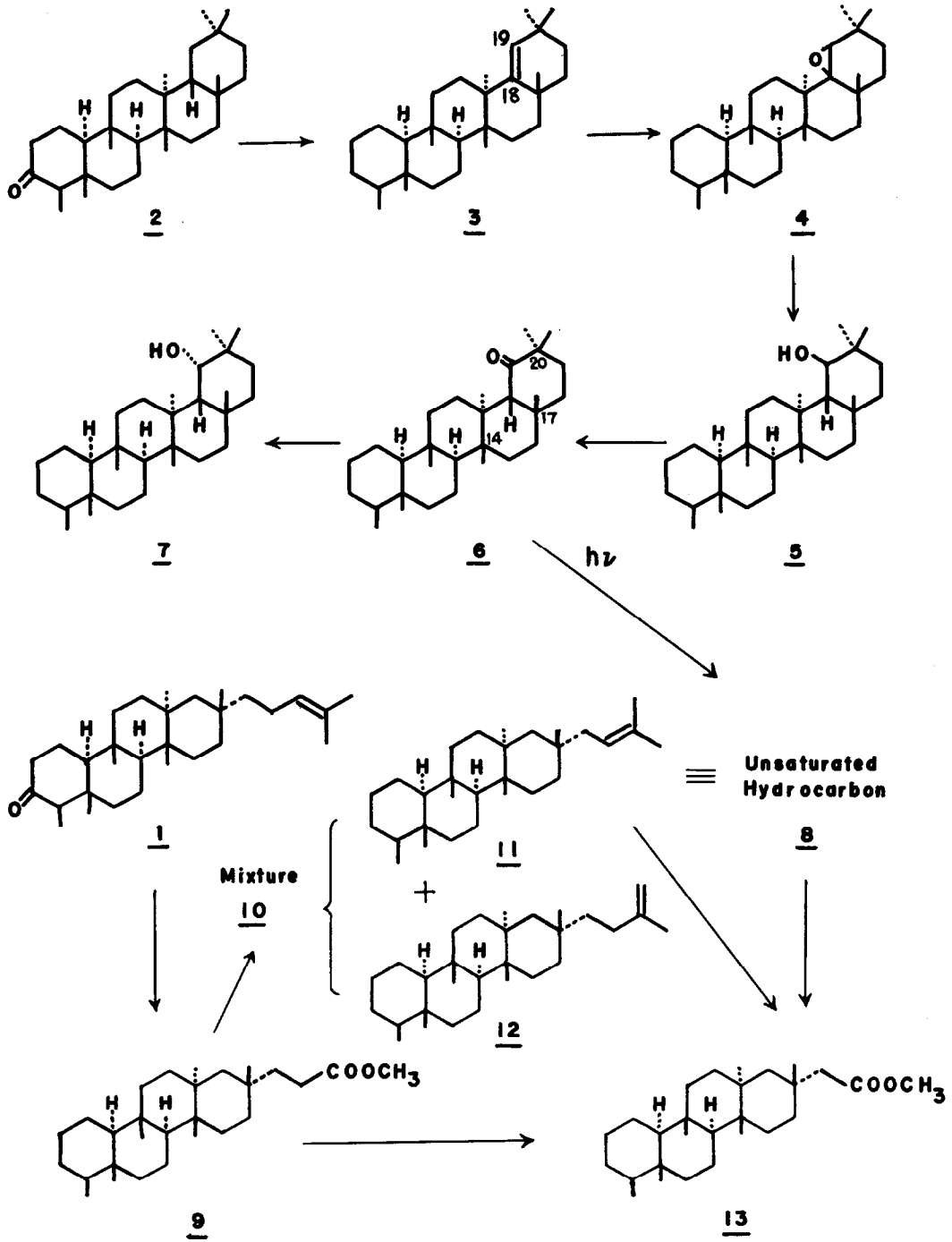
Friedelin (2) was transformed into the known 18(19)-friedelene (3)<sup>3)</sup>, which could be oxidized to the epoxy derivative (4)<sup>1b,3)</sup>. Reduction of 18 $\beta$ , 19 $\beta$ -epoxyfriedelane (4)<sup>4)</sup> with Li-EtNH<sub>2</sub>-t-BuOH gave 19 $\beta$ -hydroxyfriedelane (5)<sup>5)</sup>, C<sub>30</sub>H<sub>52</sub>O<sup>6)</sup>, m.p. 208.5 - 209.5°,  $\nu_{OH}$  3450 cm<sup>-1</sup>, NMR:  $\delta$  = 3.70 (1H, doublet, J = 6 Hz, C- $\overset{OH}{\underset{C}{|}}-\overset{C}{|}-\overset{C}{|}-C$ , in CDCl<sub>3</sub>), [ $\alpha$ ]<sub>578</sub> + 11° ( $c$  = 1.9, in CHCl<sub>3</sub>). Dehydration with phosphorus pentachloride afforded 18(19)-friedelene (3) in good yield<sup>7)</sup>, confirming that no skeletal rearrangement had occurred in the reduction of 4 to give 5. The location of the hydroxyl group at C<sub>19</sub> (not at C<sub>18</sub>) of 5 is deduced from the NMR data. The oxidation of 5 with Jones' reagent yielded 19-oxofriedelane (6)<sup>8)</sup>, C<sub>30</sub>H<sub>50</sub>O, M<sup>+</sup> 426, m.p. 235°,  $\nu_{C=O}$  1685 cm<sup>-1</sup> 9), NMR:  $\delta$  = 2.20 (1H, singlet, in CDCl<sub>3</sub>), ORD and CD: positive Cotton curves. This ketone (6), when treated with lithium aluminum hydride, furnished 19 $\alpha$ -hydroxyfriedelane (7)<sup>10)</sup>, C<sub>30</sub>H<sub>52</sub>O, m.p. 233-234°,  $\nu_{OH}$  3750 cm<sup>-1</sup>, NMR:  $\delta$  = 3.78 (1H, doublet, J = 8 Hz, in CDCl<sub>3</sub>), [ $\alpha$ ]<sub>578</sub>

+ .17° ( $c = 1.0$ , in  $\text{CHCl}_3$ ). Ketone 6, however, was recovered unchanged from the following reactions: Baeyer-Villiger and Schmidt reactions, oximation, enol-acetylation, enol-benzoylation and alkaline oxidation with potassium permanganate.

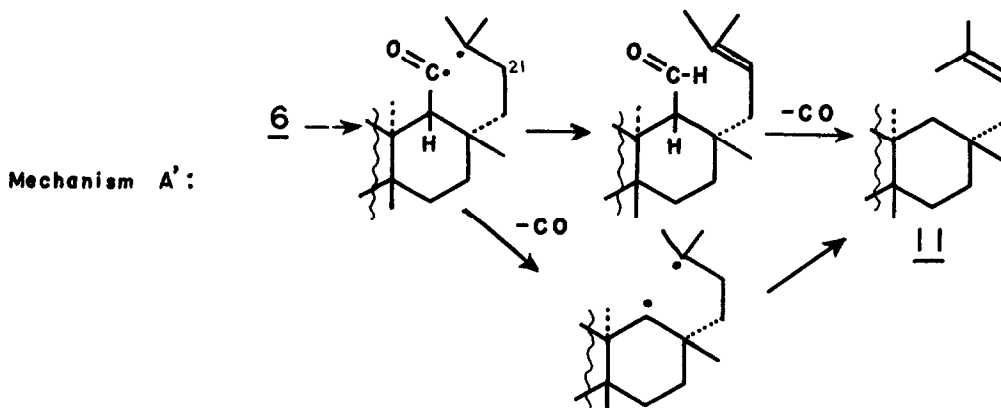
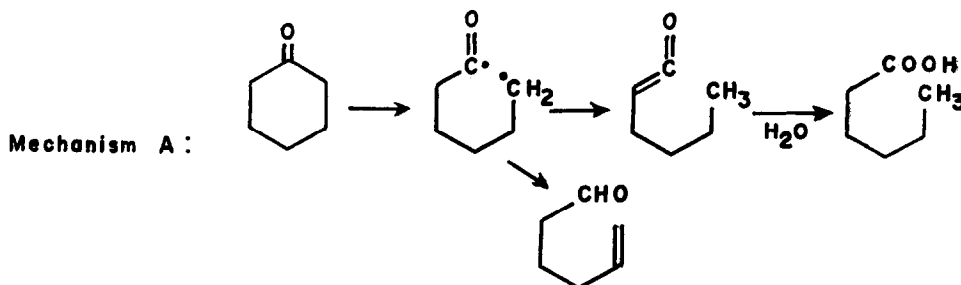
19-Oxofriedelare (6), in  $\text{AcOH-H}_2\text{O}$  (9 : 1), was heated under reflux and was irradiated under a nitrogen atmosphere using a 100 W mercury lamp. The mixture, after separation by column chromatography ( $\text{SiO}_2$  and then  $\text{SiO}_2\text{-AgNO}_3$ ), gave an unsaturated hydrocarbon (8)<sup>11</sup>, m.p. 115 - 117°,  $M^+$  398, NMR:  $\delta = 5.18$  (1H, broad singlet, in  $\text{CDCl}_3$ ), and an unidentified carboxylic acid. The hydrocarbon (8) was identical (IR, NMR, GLC, TLC and mass spectrometry) with norshionene (11),  $\text{C}_{29}\text{H}_{50}$ ,  $M^+$  398, m.p. 120 - 121°, IR:  $835\text{ cm}^{-1}$ , NMR:  $\delta = 5.18$  (1H, broad singlet, in  $\text{CDCl}_3$ ), synthesized from shionone (1) via methyl trinorshionanoate (9)<sup>1</sup>. The presence of iso-norshionene (12) (IR:  $885\text{ cm}^{-1}$ ) together with norshionene (11) was noted in the hydrocarbon mixture (10) obtained by Grignard reaction on 9, followed by dehydration. The separation of 11 from the mixture (10) was carried out by chromatography on  $\text{SiO}_2\text{-AgNO}_3$ .

Furthermore, the unsaturated hydrocarbon (8) was oxidized ( $\text{CrO}_3\text{-AcOH-H}_2\text{O}$ ) to give after methylation methyl tetranorshionanoate (13),  $\text{C}_{27}\text{H}_{46}\text{O}_2$ ,  $M^+$  402, m.p. 123.5 - 124°,  $[\alpha]_{578} + 3^\circ$  ( $c = 1.4$ , in  $\text{CHCl}_3$ ), identical (m.p. and mixed m.p.,  $[\alpha]_{578}$ , IR, NMR, GLC, TLC and mass spectrometry) with the authentic sample obtained from methyl trinorshionanoate (9) by the Barbier-Wieland procedure<sup>1</sup>. The same ester (13) was also formed on methylation of an acidic fraction obtained by oxidation of hydrocarbon mixture (10).

Photochemical cleavage of cycloalkanones yields a ketene or an unsaturated aldehyde, following mechanism "A" <sup>12</sup>. In the presence of water, this ketene gives a saturated carboxylic acid<sup>12</sup>. Irradiation of steroids with an angular aldehyde group results in decarbonylation, to yield the corresponding norsteroids<sup>13</sup>. The formation of norshionene (11) from 6 could be interpreted by the mechanism "A' ". An acyl radical formed by irradiation of 6 abstracts a hydrogen at  $\text{C}_{21}$  to yield an unsaturated aldehyde. Subsequent decarbonylation would lead to 11. An alternative explanation which involves the direct decarbonylation accompanied by migration of a hydrogen to form 11 would also be applicable.



The transformation of friedelin (2) into methyl tetranorshionanoate (13) was thus achieved. Together with evidence described in the preceding communication, the above correlation now established between friedelin and shionone leads unambiguously to the structure and stereochemistry of shionone (1). The structure 1 of shionone is entirely in agreement with the modern biogenetical theory<sup>14)</sup> of higher terpenoids, which was in fact used to derive it initially<sup>1)</sup>.



## REFERENCES

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 b- Y. Tanahashi, Y. Moriyama, T. Takahashi, F. Patil, J.-F. Biellmann and G. Ourisson, ibid., 1670 (1966). And the references cited therein.
- 2) T. Takahashi, Y. Moriyama, Y. Tanahashi and G. Ourisson, Tetrahedron Letters, preceding communication.

- 3) V. V. Kane and R. Stevenson, Chem. & Ind., 1243 (1960); Tetrahedron, 15, 223 (1961). F. Kohen and R. Stevenson, J. Org. Chem., 30, 2479 (1965).
- 4) The stereochemistry of the epoxy ring should be  $\beta$ . The  $\alpha$  configuration may be excluded because of the bowsprit-flagpole interactions due to 14 $\beta$ , 17 $\beta$  and 20 $\beta$  methyl groups.
- 5) The configuration at C<sub>18</sub> of 5 would be the same (18 $\beta$ -H) as in 6.
- 6) Satisfactory microanalyses were obtained for all new compounds.
- 7) The corresponding dehydration of the 19 $\alpha$ -OH isomer (7) gave 18(19)-friedelene (3) (in ca. 3% yield), together with other unidentified compounds formed probably by skeletal transformations.
- 8) The ketone 6 is stable to an alkaline treatment; this favors a 18 $\beta$ -H configuration (ring junctures C/D/E: trans-anti-cis) for 6. The 18 $\alpha$ -H isomer (trans-syn-trans) is considered to be much less stable than the 18 $\beta$ -H isomer. Cf. E. L. Eliel, Stereochemistry of Carbon Compounds, p. 282, McGraw-Hill, New York (1962).
- 9) The low wave number observed could be interpreted by steric environments which cause a deformation of the carbonyl group to diminish the C=O double bond character.
- 10) The formation of 7 may be well illustrated by attack of the reagent from the less hindered  $\beta$  side to give the 19 $\alpha$ -OH isomer; this furnishes a further evidence which supports the 18 $\beta$ -H configuration for 6.
- 11) No iso-norshionene (12) was found (GLC and TLC). Other unidentified hydrocarbons were also isolated.
- 12) O. L. Chapman, in W. A. Noyes Jr., G. S. Hammond and J. N. Pitts Jr., ed., Advances in Photochemistry, Vol 1, pp. 366-370, Interscience, New York (1963). P. Bladon, W. McMeekin and I. A. Williams, Proc. Chem. Soc., 225 (1962). E. L. Ghisalberti and P. R. Jefferies, Tetrahedron Letters, 6323 (1966).
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