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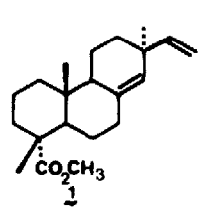
BIOMIMETIC ROUTE TO THE STROBANE SKELETON FROM METHYL PIMARATE

N.SAM, M.TARAN[a], M.PETRAUD[b], B.BARBE[b] and B.DELMOND*

Institut du Pin-Laboratoire de chimie organique et organométallique associé au CNRS (U.R.A.35)
Université de Bordeaux I -351, Cours de la Libération -33405 TALENCE Cédex (France).

ABSTRACT: From methyl pimarate a pimarane-strobane rearrangement in diterpene series is reported. This interconversion provides a biomimetic access to strobane derivatives.

In connection with our previous studies[1] dealing with biomimetic conversions in the diterpene field, the pimarane-strobane skeleton rearrangement has been investigated.



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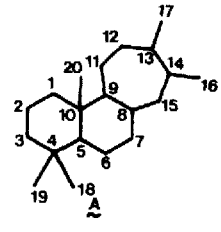
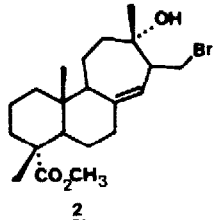


A

Reaction of methyl pimarate 1 with bromine in THF/H_2O solution in the presence of sodium bicarbonate for ten minutes at 0°C resulted in a mixture of compounds 2 - 5 (yield 90%) separated by liquid chromatography on desactivated alumina (petroleum ether / ether 8:2).



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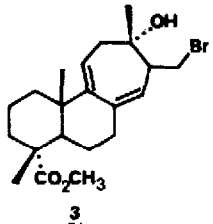

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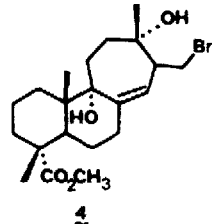

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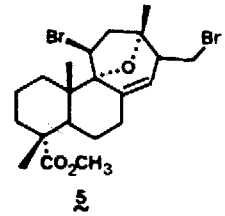

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[a] U.E.R. des Sciences Pharmaceutiques- Université de Bordeaux II.

[b] Centre d'Etudes Structurales et d'Analyses des Molécules Organiques, Université de Bordeaux I.

NMR ^1H (200 MHz); δ (ppm) :

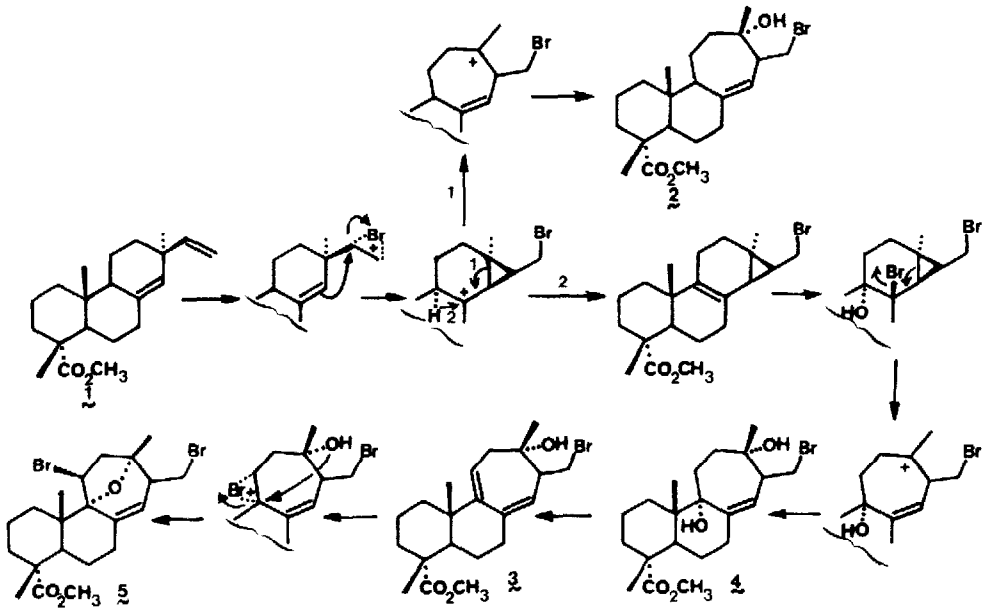
2 (***41%***) 0.91 (s, CH_3), 1.00 (s, CH_3), 1.10 (s, CH_3), 3.07 (m, H-14), 3.15 and 3.70 (m, CH_2Br), 3.58 (s, CO_2CH_3), 4.94 (m, H-15).

3 (***18%***) 1.01 (s, CH_3), 1.05 (s, CH_3), 1.19 (s, CH_3), 3.07 (m, H-14), 3.21and 3.35 (m, CH_2Br), 3.62 (s, CO_2CH_3), 5.47 (m, H-15), 5.71 (m, H-11).

4 (**5%**) 0.97 (s, CH_3), 1.02 (S, CH_3), 1.14 (s, CH_3), 2.90 (m, H-14), 3.20 and 3.68 (m, CH_2Br), 3.59 (s, CO_2CH_3), 5.05 (m, H-15).

5 (***11%***) 1.03 (s, CH_3), 1.23 (s, CH_3), 1.31 (s, CH_3), 2.14 (m, H-12), 2.8 (m, H-14), 3.0 and 3.37 (m, CH_2Br), 3.65 (s, CO_2CH_3), 4.29 (t, CHBr), 5.65 (m, H-15).

The tetracyclic structure of compound **5** was assigned on the basis of ^{13}C NMR including 2D experiments[2] . In particular, the location of the bromine atoms was determined from a 2D - heteronuclear ^{13}C-^1H chemical shift correlation[3]. The configuration α for the ether bridge between C-9 and C-13 could be inferred from the upfield shift observed on C-5 due a γ-gauche interaction with the oxygen atom[4]. The formation of these products can probably be explained by a homoallylic cyclopropyl-carbinyl rearrangement[5] from the bromohydrin precursor according the following scheme :



This reaction constitues a biomimetic route to the strobane skeleton from methyl pimarate; few examples of such a rearrangement have been described[6].

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