
The molecular rearrangement induced by acid treatment of triacetate alcohol 4 gave uruapane 5, while 6, the C(3)-stereoisomer of 4, after two consecutive Wagner-Meerwein rearrangements followed by two 1-2-hydride migrations, afforded (4R,5R,7S,8S,9S,10S,11S)-1,8,9-triacetoxojiquilp-3(12)-ene (7), which possesses a new hydrocarbon skeleton. The structure of the new substances were elucidated by 1D and 2D NMR data in combination with X-ray diffraction analyses of the uruapane, longipinane and juquilpane derivatives 5, 6 and 14, respectively. Molecular modeling at the ab initio level was used to study the reaction mechanism, while deuterium labeling was employed to confirm the C-C bond migrations and the hydride shifts.