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STEREOCHEMISTRY OF MOLLUGOGENOL-A AND MOLLUGOGENOL-E, THE TRITERPENOID SAPOGENOLS FROM *MOLLUGO HIRTA*

MANASH KUMAR CHOUDHURY and PARUL CHAKRABARTI

Department of Chemistry, Bose Institute, Calcutta 9, India

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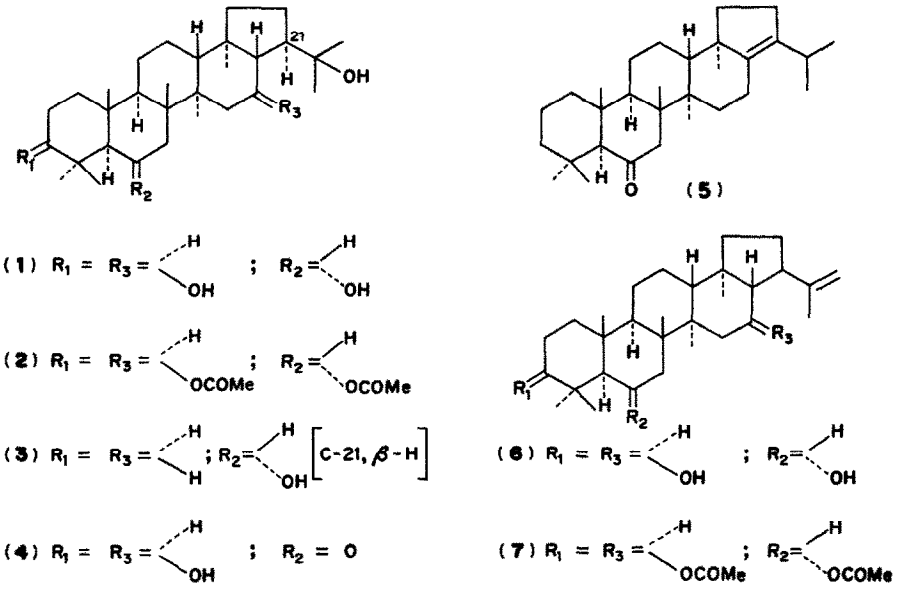
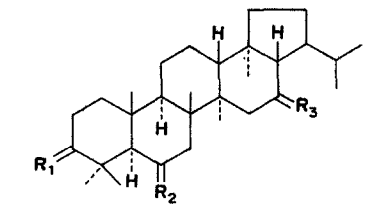
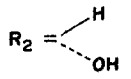
Key Word Index—*Mollugo hirta*; Ficoidaceae; pentacyclic triterpene; stereochemistry of the hydroxyisopropyl side chain; mollugogenol-A; mollugogenol-E.

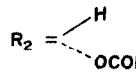
In an earlier communication [1], the structure of mollugogenol-A, a new triterpenoid sapogenin isolated from *Mollugo hirta*, was proposed as 3β,6α,16β,22-tetrahydroxyisohopane (**1**) on the basis of the spectral analysis and chemical reactions. Mollugogenol-A was finally degraded to zeorininone (**5**), a degradation product of zeorin (**3**), a triterpene of the hopane series. However this work did not determine the sterochemistry of the hydroxyisopropyl side chain at C-21.

Hydrogenolysis of the side chain of mollugogenol-A in the presence of hydrogen and PtO_2 in acetic acid was found to be very slow and furnished mainly, unreacted product together with a small amount of the saturated compound (**8**). Mollugogenol-A therefore behaved like a member of the isohopane rather than of the hopane series [2]. However, there was no conclusive chemical proof regarding the stereochemistry of the hydroxyisopropyl side chain. With a view to obtaining more direct evidence, the problem has been re-investigated and it has been possible to convert mollugogenol-A to 6-ketoisohopane (**11**) which has clearly established the β-orientation (isohopane) [3] of the side chain. Thus the structure of mollugogenol-A has now been finally established as (**1**) and consequently that of mollugogenol-E [4] as (**4**), the oxidation product of which was correlated with the oxidation product of mollugogenol-A. Mollugogenol-A fur-

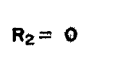




(8) $R_1 = R_3 =$  ; $R_2 =$

(9) $R_1 = R_3 =$  ; $R_2 =$ 

(10) $R_1 = R_2 = R_3 = O$

(11) $R_1 = R_3 =$  ; $R_2 = O$

nished two acetates, namely the monohydroxy triacetate (**2**), and the dehydro triacetate (**7**). The latter responded to the tetranitromethane test indicating the presence of unsaturation. The presence of the isopropenyl group (Me–C(=CH_2)–) in (**7**) was shown by its IR spectrum [1735 and 1240–1250 (acetoxy), 1640 and 900 cm^{-1} (=CH_2)] but there was no band for a hydroxyl group. The presence of the tertiary hydroxyl group in (**2**) was shown by the band at 3500 cm^{-1} in its IR spectrum.

The dehydro triacetate (**7**) was separated from monohydroxy triacetate (**2**) by column chromatography. Catalytic hydrogenation of (**7**) gave the saturated triacetate (**9**). This compound had no bands at 1640 and 900 cm^{-1} (=CH_2) in its IR spectrum and it did not give a pale yellow colouration with tetranitromethane. Moreover the NMR spectrum of this compound (**9**) showed six sharp singlets in the region δ 0·78–1·45 for 8 methyl groups and 2 sharp singlets at δ 2·03 (3H) and 2·07 (6H) for 3 acetoxy groups ($\underline{CH_3}CO \cdot O$). There was no sharp singlet at δ 1·69 (3H, $\underline{CH_3}$–C(=CH_2)–) or the broad singlet at δ 4·62 (2H, Me–C(=$\underline{CH_2}$)–) which are observed in the case of the unsaturated acetate (**7**) [1]. This compound on saponification gave a triol (**8**) as shown by the IR band at 3520 cm^{-1}. The triol on Sarett oxidation gave a triketone (**10**). It showed a band at 1715 cm^{-1} for a carbonyl group but no band for any free hydroxyl group. Finally Wolff–Kishner reduction of the triketone (**10**) produced a compound which was found to be identical with 6-keto-isohopane (**11**) by comparison (mmp, TLC and superimposable IR spectrum) with an authentic sample.

EXPERIMENTAL

Acetylation of mollugogenol-A. Mollugogenol A (1 g) was heated with Ac_2O (20 ml) and Py (5 ml) for 1 hr and the product worked up in the usual way. Crude acetate showed 2 spots on Si gel TLC which were less polar than mollugogenol-A. The product was dissolved in C_6H_6 and adsorbed onto a column of Si gel (100 g). Elution with C_6H_6 gave a colourless compound (430 mg) which was crystallized from MeOH, mp 235–37° (**7**) (Found: C, 73·45; H, 9·47; requires: C, 73·93; H, 9·65%). Further elution with $C_6H_6/CHCl_3$ (2:1) gave a glassy colourless product (490 mg) which was crystallized from aq. MeOH, mp 230–32° (**2**). (Found: C, 71·58; H, 9·92; $C_{36}H_{58}O_7$ requires: C, 71·73; H, 9·70%). MW 602 (M^+).

Catalytic hydrogenation of the 22-dehydro triacetate (7) to the 22-deoxy triacetate (9). Dehydromollugogenol-A triacetate (400 mg) was dissolved in EtOH (20 ml) and shaken in an atmosphere of H_2 at room temp. and atm pres with Adam's catalyst (50 mg). The dehydro compound consumed 1 mol of H_2. The soln was filtered, the solvent distilled off and residue (**9**) crystallized from MeOH, mp 219–20° (300 mg); $[\alpha]_D^{27}$ + 62·7° ($CHCl_3$). The homogeneity of the hydrogenation product was checked by TLC on Si gel impregnated with $AgNO_3$ (12·5%). The product was less polar than the unsaturated compound. (Found: C, 73·41; H, 10·12; requires: C, 73·68; H, 9·96%).

Saponification of the triacetate (9) to the triol (8). The triacetate (500 mg) was dissolved in EtOH (20 ml) and alcoholic KOH (4%, 20 ml) was added; the mixture was kept overnight at room temp. The resulting triol (**8**) (400 mg) obtained after filtration through a column of Si gel (10 g) was crystallized from EtOH, mp 254–58°. (Found: C, 77·93; H, 11·52; requires: C, 78·21; H, 11·38%).

Sarett oxidation of triol (8) to triketone (10). A cold soln of triol (400 mg) in Py (6 ml) was added to a slurry of CrO_3–Py complex (800 mg CrO_3 and 20 ml Py) at 0° and left overnight at room temp. The product (**10**) was purified by chromatography over Si gel (15 g) and crystallized from MeOH (295 mg), mp 270–75° (decomp.) (Found: C, 79·51; H, 10·37; requires: C, 79·25; H, 10·20%).

Wolff–Kishner reduction of triketone (10). A soln of triketone (900 mg) in a mixture of absolute EtOH (60 ml) and diethylene glycol (30 ml) was refluxed with hydrazine hydrate (85%, 30 ml) for 1 hr on a steam bath. Solid KOH (8 g) was then added and the reaction mixture again refluxed for another 15 min. An appreciable amount of solvent was distilled off under red pres and the mixture heated at 200° for 3 hr. The product was worked up in the usual way, purified by Si gel (25 g) column chromatography and crystallized from MeOH (565 mg), mp 203–4°; identical with authentic 6-ketoisohopane (**11**) by mmp, TLC and superimposable IR.

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