Acid hydrolysis of the compound gave dalpanol, identified by m.p., m.m.p., co-chromatography, UV and superimposable IR spectra with an authentic sample. The sugar from the aq. mother liquor was identified as glucose by PC. Acetylation gave the acetate, $C_{37}H_{42}O_{16}$, m.p. 98°, λ_{max} (MeOH): 218, 236, 244 sh. and 294 nm. ν_{max} (KBr): 1765, 1670 cm⁻¹.

Comments. Dalpanol-O-glucoside is the second rotenoid glycoside reported, the first being amorphin from the seeds of *Amorpha fruticosa.*⁹

Acknowledgements—Thanks are due to Professor M. V. Bhatt (Bangalore) for the NMR spectra, Professor O. R. Gottlieb for a sample of caviunin, and Dr. D. Adinarayana for a sample of the aglycon of dalpatin and IR spectra.

⁹ CLAISSE, J., CROMBIE, L., and PEACE, R. (1964) J. Chem. Soc. Suppl. No. 2, 6023.

Phytochemistry, 1973, Vol. 12, pp. 3004 to 3006. Pergamon Press. Printed in England.

LORANTHOL: A NEW PENTACYCLIC TRITERPENOID FROM LORANTHUS GREWINKII

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(Received 17 May 1973. Accepted 2 July 1973)

Key Word Index-Loranthus grewinkii; Loranthaceae; structure elucidation; MS; triterpenoids; loranthol.

Abstract—Loranthol (VIII) has been shown by chemical and physical methods to be lup-20(30)-en- 3β , 7β -diol, a new triterpenoid of the lupane series. The stereochemistry was established by its degradation to the parent hydrocarbon, lup-20(30)-ene.

SIDDIQUI et al.¹ have reported a new triterpenoid, 'loranthol', from berries of *Loranthus* grewinkii, a parasite found widely in West Pakistan on pear, apricot and almond trees. The gum from these berries is highly valued in the indigenous system of medicine as a general tonic, relaxant and laxative.

Loranthol forms a diacetyl and a dibenzoyl derivative.¹ It must therefore bear two hydroxyl groups. Its formula as $C_{30}H_{50}O_2$ was confirmed by low and high resolution MS. MS also suggested the presence of a lupane type of skeleton.² This conclusion was further supported by the similarity of the IR spectrum of loranthol with those of betulin³ and

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¹ KHAN, N. H., AMEEM, M. and SIDDIQUI, S. (1958) Pakistan J. Sci. and Ind. Res. 1 (3), 191.

² BUDZIKIEWICZ, H., WILSON, J. M. and DJERASSI, C. (1963) J. Am. Chem. Soc. 85, 3688.

³ Elseviers Encyclopaedia of Organic Chemistry, Suppl. 568, 11335.

lupeol.⁴ Jones oxidation of loranthol afforded the corresponding diketone, m.p. 200–202°. Wolff-Kishner reduction of the diketone afforded lup-20(30)-ene, m.p. 163°, conclusively demonstrating the nature of the skeleton.

In the MS were major fragments of m/e = 236 and 223, corresponding to $C_{15}H_{24}O_2$ (I) and $C_{14}H_{23}O_2$ (II) respectively by cleavages across ring C. This suggested that both hydroxyl groups were located in rings A and/or B. The occurrence of non-oxygen containing fragments with rings D and E intact, present at m/e = 217, 203, 189 and 175 corroborated such a conclusion. These were shown by high resolution MS to be due to the ions $C_{16}H_{25}$ (III), $C_{15}H_{23}$ (IV), $C_{14}H_{21}$ (V) and $C_{13}H_{19}$ (VI) respectively. The fragment $C_9H_{15}O$ (VII), consisted of ring A bearing a single hydroxyl group, strongly suggesting that the two hydroxyl groups were located separately in rings A and B.



The NMR spectrum of loranthol proved particularly informative. The seven methyl groups appeared as sharp singlets at 0.76, 0.78, 0.80, 0.97, 1.02, 1.05 and 1.66 δ values. These signals were assigned to the 23, 28, 24, 25, 27, 26 and 29 methyls respectively on the basis of known positions of methyl groups in such triterpenoids.⁵ The two olefinic protons of the isopropenyl side chain on ring E resonated at 4.56 and 4.68 δ values respectively (J_{gem} 1.7 Hz). Two four-line patterns centred at 3.18 and 3.81 δ were also apparent. These were assigned to the protons geminal to the hydroxyl functions.

The two hydroxyl groups could not be situated in a vicinal disposition, since the resultant signals of the protons geminal to the hydroxyl groups would not afford the observed splitting pattern. This was confirmed by attempted oxidation of loranthol with sodium metaperiodate which failed to give the corresponding dialdehyde, and starting material was recovered. A 1,3-disposition of the two hydroxyl groups in ring A was also not possible since the physical properties of loranthol and its diacetate did not correspond with any of the four possible diastereoisomeric lup-20(30)-en-1,3-diols.⁶ Proof for this came from the

⁴ Elseviers Encyclopaedia of Organic Chemistry, Suppl. 575, 11155.

⁵ LEHN, J.-M. and OURISSON, G. (1962) Bull. Soc. Chim. Fr. 1137.

⁶ GANGULY, A. K., GOVINDACHARI, T. R., MOHAMED, P. A., RAHIMTULLA, A. D. and VISWANATHAN, N. (1968) Bull. Nat. Inst. Sci. India, 37, 77.

UV spectrum of the diketone obtained by Jones oxidation of loranthol. The characteristic UV absorptions typical of β -ketoenolates, were found to be absent.



Comparison of the NMR spectrum of loranthol with that of lupeol showed that one of the downfield protons, centred at 3.18 δ , possessed an identical chemical shift and splitting pattern (J_{aa} 10 Hz, J_{ae} 5.5 Hz). This must therefore be the C-3 proton, and the hydroxyl group attached to this carbon atom must have a β (equatorial) disposition. The second hydroxyl group was located at C-7 in an equatorial disposition, since the proton at C-7 resonated as a four-line pattern centred at 3.81 δ (J_{aa} 10 Hz, J_{ae} 5.5 Hz). A location of the hydroxyl group at C-6 would have involved an additional splitting of the quartet of the geminal proton by the C-5 methine proton. The ease of acetylation of the diol, and of the Wolff-Kishner reduction of the dione further supported the conclusion that the second hydroxyl group was located at C-7 and not C-6 which is a more hindered position. Finally the MS showed the fragment VII which bore only one hydroxyl group, strongly suggesting that the second hydroxyl group was at C-7 and not at C-6.

In view of this evidence the structure of loranthol is suggested to be lup-(30)-en- 3β , 7β -diol (VIII).

EXPERIMENTAL

Loranthol (VIII). Loranthol was obtained as a colourless crystalline compound according to the procedure described by Siddiqui *et al.*, ¹ m.p. 224–226°; (Found: C, 81·4; H, 11·4. $C_{30}H_{50}O_2$ requires: C, 81·39; H, 11·38%) $[a]_D^{29} = +4.50$ (CHCl₃); IR bands similar to lupeol; ¹ NMR spectrum (CDCl₃) 8 [H]*m*: 0.76[3H]*s*, 0.78[3H]*s*, 0.80[3H]*s*, 0.97[3H]*s*, 1.02[3H]*s*, 1.05[3H]*s*, 1.66[3H]*s*, (assigned to 23, 28, 24, 25, 27, 26 and 29 methyls respectively), 4.56[1H]*m*, 4.68[1H]*m* (C-30 olefinic protons), 3.18[1H]*m* (C-3 proton), 3.81[1H]*m* (C-5 proton); MS: m/e = 442.3822 (M⁺, $C_{30}H_{50}O_2$), 427.3557 (M⁺-15, $C_{29}H_{47}O_2$), 409.3461 ([M⁺-Me]-H₂O, $C_{25}H_{45}O_1$), 332.2705 ($C_{22}H_{36}O_2$), 331.2622 ($C_{22}H_{35}O_2$), 249.1837 ($C_{16}H_{25}O_2$), 236.1768 ($C_{15}H_{24}O_2$, I), 223.1683 ($C_{14}H_{23}O_2$, II), 217.1955 ($C_{16}H_{25}$, III), 203.1789 ($C_{15}H_{23}$, IV), 189.1649 ($C_{14}H_{21}$, V), 175.1484 ($C_{13}H_{19}$, VI), 139.1126 ($C_{9}H_{15}O$, VII).

Lup-20(30)-en-3,7-dione. To loranthol (VIII), 0.032 g (0.074 mmole) dissolved in 1 ml acetone, chromic acid (0.052 g), [standard solution prepared by dissolving CrO_3 (2.6 g) in conc. H_2SO_4 (2.3 ml) and diluting with H_2O to 10 ml] was added. The solution was stirred for 10 min, poured into 100 ml of cold H_2O and extracted with 3 × 10 ml portions of Et₂O. The Et₂O extracts were dried, filtered and evaporated to afford a colourless crystalline solid (0.025 g); m.p. 200–202°; (Found: C, 82·1; H, 10·2. $C_{30}H_{46}O_2$ requires: C, 82·2; H, 10·5%); NMR (CDCl₃) [H]m: 0.80[3H]s, 1.03[6H]s, 1.06[3H]s, 1.14[3H]s, 1.33[3H]s, 1.68 [3H]s 4·58[1H]m, 4·68[1H]m; MS, $m/e = 438(M^+), 423(M^+-15), 370, 327, 247, 234, 205, 130, 109, 95.$

Lup-20(30)-ene. Lup-20(30)-en-3,7-dione (0.021 g) was dissolved in diethylene glycol (2 ml) and hydrazine hydrate (0.5 ml). The solution was refluxed in N₂ for 0.5 hr (internal temp. 180–200°). The solution was cooled, powdered KOH (0.5 g) added and the solution heated under N₂ to 180° when H₂O and excess hydrazine were allowed to distil off (*ca*. 0.5 hr), and the remaining solution was heated to 200° for 3 hr. The solution was allowed to cool, diluted with H₂O (20 ml) and extracted with light petrol. b.p. 30–40° (3 × 10 ml). The combined light petrol. extracts were washed with saturated brine solution, dried and evaporated to afford a colourless gum, 0.01 g. The gum was chromatographed on a small silicic acid column to afford a crystalline solid, 0.012 g, m.p. 163°, identical with authentic lup-20(30)-ene.