Phytochemistry, 1968, Vol. 7, pp. 333 to 334. Pergamon Press. Printed in England

SHORT COMMUNICATION

TRITERPENOID CONSTITUENTS OF *GRISELINIA SCANDENS*

M. SILVA* and M. BALOCCHI
Departamento de Botánica, Universidad de Concepción, Chile

and

P. G. SAMMES
Chemistry Department, Imperial College, London, S.W.7

(*Received* 21 *August* 1967)

DURING a current project dealing with Chilean flora,[1] we had occasion to examine *Griselinia scandens* (R. et P.) Taub., a *Cornaceae*. The alcoholic extract of the dried, pulverized and defatted plant yielded a water-soluble glycosidic fraction. Acid hydrolysis of this material yielded a mixture of sapogenins containing A_1 barrigenol[2] and oleanolic acid which were characterized through their derivatives and by mass spectrometric measurements.

When this work was in progress Itô *et al.*[3] and Errington *et al.*[4] published, independently, a revised structure for A_1 barrigenol, as: 3β, 15α, 16α, 22α, 28-pentahydroxyolean-12-ene, instead of that proposed earlier.[2]

EXPERIMENTAL

Melting points were uncorrected and determined on a Kofler block. The microanalyses were performed by Dr. A. Bernhardt, Mülheim, Germany. Nmr spectra were determined on a Varian HA-100 spectrometer using deuterochloroform as solvent and tetramethylsilane as an internal reference. Mass spectra were performed with an AEI MS9, double focusing mass spectrometer. The alumina used was aluminium oxide active neutral Merck. Silica gel (Kieselgel) was used for TLC.

Extraction and Isolation of the Sapogenin

Leaves of *Griselinia scandens* collected in March (summer) 1966 near Concepción, Chile, were dried. 3470 g of dried powder were extracted in a Soxhlet with light petroleum (b.p. 65–75°) to exhaustion. The defatted material was then extracted with benzene. From the light petroleum and benzene extracts, two compounds were isolated which showed no triterpenoid characteristics; both appeared to be polymethylenic alcohols and were not further studied.

The extracted material was again dried, and extracted with ethanol. The dark green solution was concentrated, acidified with HCl to render it approximately 2·5 N, and refluxed for 7 hr. The precipitate formed on dilution with water was collected, washed free of acid and dried (131 g). The filtrate showed a slightly positive alkaloid reaction. The precipitate was extracted with ether (Soxhlet), and the crude extract chromatographed over alumina (Merck, Grade III; 30 g). Exhaustive elutions with benzene, ethyl acetate and ethanol yielded 2·1 g of a product *A* m.p. 284°, which was found to be a mixture of two compounds (TLC).

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* To whom inquiries should be sent.

[1] M. SILVA, *J. Pharm. Sci.*, in press.

[2] A. R. H. COLE, D. T. DOWNING, J. C. WATKINS and D. E. WHITE, *Chem. & Ind.* 254 (1955).

[3] S. ITÔ, T. OGINO, H. SUGIYAMA and M. KODAMA, *Tetrahedron Letters* 2289 (1967).

[4] S. G. ERRINGTON, D. E. WHITE and M. W. FULLER, *Tetrahedron Letters* 1289 (1967).

A_1 barrigenol. The product *A*, after several crystallizations from acetone, gave a compound m.p. 292° $[\alpha]_D$ 0° (pyridine, *c* 0·51), λ_{max}^{EtOH} 206 nm (ϵ 5313), ϑ_{max}^{KBr} 3350 cm.$^{-1}$ (Found: C, 73·43; H, 10·23. Calcd. for $C_{30}H_{50}O_5$: C, 73·43; H, 10·27 per cent). No melting point depression was observed upon admixture with authentic A_1 barrigenol. Further proof of identity was obtained by TLC.

A_1 barrigenol tetra-acetate. A_1 barrigenol on acetylation with pyridine-acetic anhydride at room temperature gave, after crystallization from acetone, the acetate m.p. 162–166°, $[\alpha]_D - 11{\cdot}3°$ (chloroform, *c* 0·7), $\vartheta_{max}^{CHCl_3}$ 3450, 1739 and 1250$^{cm^{-1}}$. Mass spec. 658 (M^+ 5 per cent), 598 (46), 583 (11), 390 (5), 317 (6), 249 (13), 190 (41), 175 (12). This spectrum showed a fragmentation pattern typical of a Δ^{12}oleanene.[5] The NMR spectrum indicated four methyl groups for acetyl functions.

A_1 barrigenol penta-acetate. A_1 barrigenol on acetylation at 100° gave a compound m.p. 248–258°, $[\alpha]_D - 26{\cdot}3°$ (chloroform, *c* 1·3), exhibiting no melting point depression upon admixture with A_1 barrigenol penta-acetate. Further proof was obtained from comparison of mass spectral and TLC behaviour.

A_1 barrigenol tribenzoate. The benzoate prepared at room temperature had m.p. 230°, $[\alpha]_D + 33{\cdot}7°$ (chloroform, *c* 0·27).

Oleanolic acid. Since attempts to separate the less polar compound from A_1 barrigenol proved unsuccessful, product *A* (500 mg) was acetylated. Careful chromatography on deactivated alumina (30 g) with light petroleum (b.p. 65–75°), containing increasing amounts of ether, afforded oleanolic acetate (54 mg). This compound after recrystallization from ethanol had m.p. 248–250°. The NMR spectrum of this acetate showed seven methyl groups, one signal for acetate at τ 8·0, at 5·54 (a poorly resolved triplet, C-3 methine) and 4·78 (a poorly resolved triplet, one vinylic proton at C-12). The mass spectrum had characteristic signals[5] at 498 (M^+, 3 per cent), 248 (43) and 249 (13). (Found: C, 76·81; H, 9·85. Calcd. for $C_{32}H_{50}O_4$: C, 77·06; H, 10·11 per cent). No melting point depression was observed upon admixture with authentic oleanolic acetate. Further proof of the identity was obtained by TLC.

Acknowledgements—The authors are grateful to Professor O. Matthei for the botanical identification and to Professor Sho Itô and Dr. S. G. Errington for providing reference specimens.

[5] H. BUDZIKIEWICZ, C. DJERASSI and D. H. WILLIAMS, *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol. II, pp. 121–127, Holden-Day, San Francisco (1964).