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ALOE REVISITED THE STRUCTURE OF ALOERESIN A

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<u>Summary</u> - Aloeresin A, a major constituent of Cape Aloe, is shown to be 2'-O-(E)-p-coumaroyl aloesin (3) instead of <math>6'-O-(E)-p-coumaroyl aloesin (2) as accepted so fam.

Commercial aloe¹ is known to contain four major constituents, i.e. aloin A (or barbaloin)^{2,3} and aloin B (stereoisomeric anthrone C-glucosides); aloesin (<u>1</u>) (formerly aloeresin B)⁴ and aloeresin A (both 5-methylchromone C-glucosides)^{5,6}. Structure <u>2</u>, proposed by H. Wagner <u>et al.</u>⁵ for aloeresin A, has been generally taken as true⁶, although no unequivocal proof has been given so far (nor specification of the C-1' configuration). We report here that structure <u>2</u> is incorrect, at least for aloeresin A present in Cape Aloe¹, the correct one being <u>3</u>.



From several samples of Cape Aloe, using preparative HPLC (PrepPak-500/C₁₈, H₂O-MeOH 8:2), we were able to isolate large amounts of pure aloesin⁴ and aloeresin A: m.p. 148-150°C lit.⁵ 135-140°C, found C 60.38, H 5.50 calcd. for C₂₈ H₂₈ O₁₁. H₀: C 60.21; H 5.41; λ_{max}^{MeOH} nm (ϵ): 228 (34 250), 243 sh (25 900), 252 (25 000), 300 (37 960); ν_{max}^{KBr} : 3400, 1715, 1650 cm⁻¹.

Treatment of aloeresin A with NaOH under the same conditions described for deacetylating aloesin (<u>1</u>) gave deacetylaloesin (<u>1</u> with a methyl group in place of the acetonyl side-chain) and pcoumaric acid, thus confirming that aloeresin A is an O-p-coumaroyl derivative of aloesin. The following spectroscopic evidence allowed the complete structure 3 to be assigned to aloeresin A. 1 H- and 13 C-NMR spectra of both aloesin and aloeresin A⁷ (DMSO-d₆, TMS=0) showed all the signals due to the 2-acetonyl-5-methylchromone moiety (cf. ref. 4 for 1 H-NMR data). In addition, spectra of aloeresin A exhibited signals attributable to the (E)-p-coumaroyl group.

Concerning the glucose unit, it was observed that in the ¹H-NMR spectrum of aloeresin A, but not in that of aloesin (<u>1</u>), an apparent triplet (really a doublet of doublets) was present at δ 5.50 (1H, J \cong J' \cong 9Hz), which did not disappear by D₂O exchange. Spin decoupling experiments showed this triplet to be related to the doublet at δ 4.98 (1H, J=9Hz) due to the C(1') proton⁸ (the triplet becoming a doublet, J=8Hz, and the doublet a singlet).Therefore, the p-coumaroyloxy group of aloeresin A must be located at C(2'), as in <u>3</u>⁹. This is also consistent with the frequency shifts observed for ¹³C-signals of C(1'), C(2') and C(3') in going from <u>1</u> (δ , 73.5; 71.1; 78.6 respectively) to <u>3</u> (δ , 70.2; 72.3; 76.0)¹⁰

Finally, it can be pointed out that the values of J $_{H(1')-H(2')}$ (9 Hz) and J $_{13C(1')-H(1')}$ (145 Hz) indicate a β -C-glucoside linkage^{11,12} in both <u>1</u> and <u>3</u>.

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NOTES AND REFERENCES

- 1) Aloe is the dried latex of the leaves of <u>Aloe ferox</u> Miller (Liliaceae) known in commerce as Cape Aloe, or of <u>Aloe vera</u> Miller, known as Curaçao Aloe. See U.S. Pharmacopeia XX-The National Formulary XV, Marck Printing Co, Easton, Pa, 1979, p.21.
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- 8) NMR signals of anomeric protons in aromatic C-glucosides are known to fall in the range δ4.5-5.0 (e.g. at 4.77 in <u>1</u>). See R.M. Horowitz and B. Gentili, <u>Chem. Ind.</u> (London), 498 (1964).
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