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A SYNTHESIS OF ALOE-EMODIN 1,8-DI-β-D-GLUCOSIDE

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While preparing aloe-emodin 8-mono-β-D-glucoside by the hydrolysis of aloe-emodin glucoside tetraacetate formed by the reaction of aloe-emodin with acetobromoglucose[1] we have found that aloe-emodin 1,8-di-β-D-glucoside may be synthesised by increasing the reaction time and ratio of acetobromoglucose to aloe-emodin.

Aloe-emodin (200 mg) was dissolved in freshly distilled quinoline (8 ml) and to it added freshly precipitated silver oxide (1.2 g) and acetobromoglucose (750 mg) dissolved in benzene (5 ml) and shaken for 28 hours at room temperature. The aloe-emodin diglucoside octoacetate was extracted and hydrolysed to aloe-emodin diglucoside by established methods.[1] The crude diglucoside was crystallised from methanol to give yellow crystals (70 mg).

Analytical microanalysis gave the following results:-

Found:	C; 51.53%	H; 5.17%	$C_{27}H_{30}O_{15}$
Requires (for diglucoside):	C; 54.55%	H; 5.05%	

Optical rotation: $(\alpha)_D^{20}$ in 75% acetone (c, 0.085) was - 115°.

Other properties of the prepared aloe-emodin diglucoside, compared to those of synthesised aloe-emodin 8-mono-β-D-glucoside [1] and of aloe-emodin, [2] are tabulated in Table 1.

The percentage of aloe-emodin in the prepared diglucoside and monoglucoside was found by hydrolysing the glycosides and assaying the liberated aloe-emodin[3] and glucose[4]. The amount of aloe-emodin was 39.8% in the diglucoside and 58% in the monoglucoside. (Theoretical amount of aloe-emodin in the diglucoside is 42.8% and 60% in the monoglucoside).

Thus the percentage of aloe-emodin in the molecule, the elemental analysis and differences in properties of the synthesized compound from aloe-emodin and its monoglucoside suggest that it is a diglucoside of aloe-emodin.

TABLE 1

Properties of aloe-emodin, aloe-emodin mono- and di- glucosides

	aloe-emodin	aloe-emodin monoglucoside	aloe-emodin diglucoside
Solubility in water	Insoluble	Almost Insoluble	Slightly Soluble
M.pt.	225°C	237-238°C	229°C
U.V.Spectra	(methanol)	(methanol)	(60% ethanol)
max. mμ	225(logE 4.59)	223(logE 4.42)	222(logE 4.46)
" "	256(" " 4.36)	255(" " 4.32)	260(" " 4.57)
" "	278(" " 4.03)	410(" " 3.87)	388(" " 3.92)
" "	287(" " 4.03)		
" "	430(" " 4.03)		
I.R.Spectra	cm^{-1}	cm^{-1}	
C=C (arom.)	1570	1580	1585, 1600
C=O (chelated)	1630 strong	1624 strong	-
C=O (free)	1670 weak	1661 weak	1675 strong
-OH	3400 strong	3400 strong	3400 v. strong

The position of attachment of the two glucose molecules was determined from consideration of the I.R. spectra. Aloe-emodin and its monoglucoside showed a weak absorption band at 1670 cm^{-1}, due to unbonded carbonyl groups, and strong absorption bands at 1625 cm^{-1}, indicating the presence of bonded carbonyl groups. The spectrum of the synthesised aloe-emodin diglucoside showed a much stronger absorption band at 1670 cm^{-1} and no absorption at 1625 cm^{-1} suggesting the absence of any bonded carbonyl groups in the molecule. Thus the absence of hydrogen bonding suggests that a glucose molecule is attached to each phenolic group at positions 1 and 8 in the synthesised aloe-emodin diglucoside.

We therefore suggest that the product obtained from this modified reaction is aloe-emodin 1,8-di-β-D-glucoside (I).

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