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THE COMPLETE STRUCTURE OF MATAIRESINOL MONOGLUCOSIDE*

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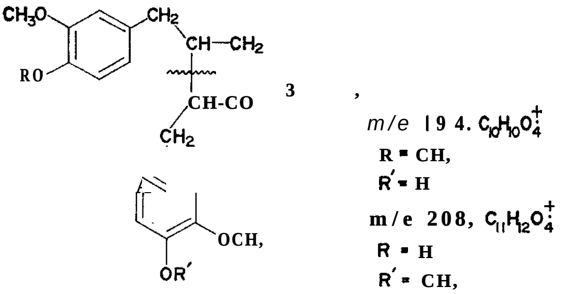
Abstract-The glucose position of matairesinol monoglucoside has been established by comparison with arctiin.

INTRODUCTION

ONE OF the components of safflower meal causing its bitter taste is matairesinol monoglucoside. At the time of the first report' of its isolation and identification the position of the glucose link to matairesinol (I) was unknown. This communication presents the complete structure of the compound as it occurs in safflower meal.



(I) R=R'=H
(II) $R{=}CH_3; R'{=}C_6H_{11}O_5$
(III) $R{=}CH_3$; R'=H
(IV) R=H; $R'{=}CH_3$
(V) $R{=}C_6H_{11}O_5$; R'=H

In order to establish the location of the glucose it was deemed necessary to relate this β-glucoside to a known glucoside. The aglycone of arctiin[2] (II), arctigenin[3] (III) is structurally similar to matairesinol, with a key difference of a methoxyl group replacing one hydroxyl group of matairesinol. If methylation of the free hydroxyl in matairesinol monoglucoside and subsequent hydrolysis produced a product identical to arctigenin (III), the glucosidic position would be established as being identical to arctiin; if the product was dissimilar, the glucosidic link would be established as the alternate.

* Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

[1] R. PALTER and R. E. LUNDIN, *Phytochem.* **9**, **4298** (1970).

[2] W. M. HEARON and W. S. MACGREGOR, *Chem. Rev. 55,975* (1955).

[3] W. M. HEARON and W. S. MACGREGOR, *Chem. Rev. 55,975* (1955).

RESULTS AND DISCUSSION

Authentic arctiin (II) was obtained and hydrolyzed with HCl to arctigenin (III). Matairesinol monoglucoside, isolated from safflower meal, was methylated[4] with CH_3 I and without purification of the methylated glucoside, acid hydrolyzed to the methylated aglycone. Both the arctigenin (III) and the matairesinol glucoside reaction product were purified by PLC. Since the quantities of both compounds were less than 10 mg, recrystallizations were not attempted.

High resolution mass spectrometry established that both compounds had the expected empirical formulas of $C_{21}H_{24}O_6$ and only negligible impurities were present. Integration of the NMR spectra showed totals of 24 protons in agreement with the mass spectral analysis.

Very slight TLC differences in R_f between the two compounds was the first indication

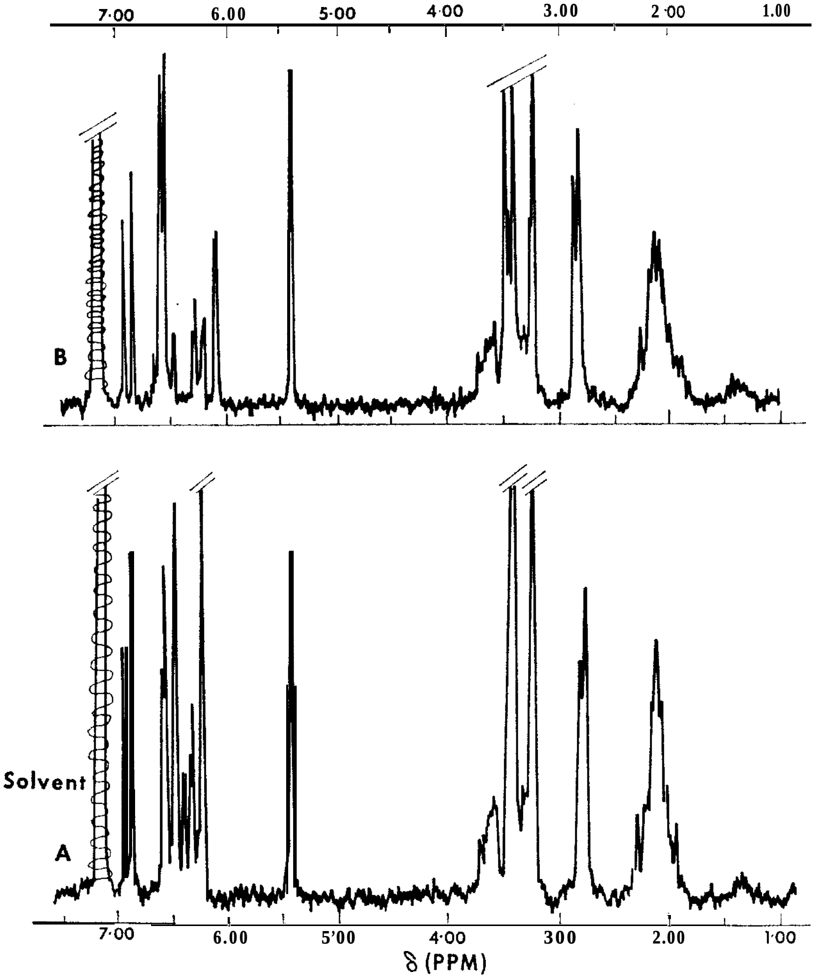


FIG. 1. 100 MHz PROTON NMR SPECTRA; 8 mg OF COMPOUND IN BENZENE-d_6. (A) AUTHENTIC ARCTIGENIN; (B) METHYLATED AGLYCONEOF MATAIRESINOL MONOGLUCOSIDE.

[4] R. M. SAUNDERS and H. G. WALKER, JR., *Cereal Chem.* 46, 85 (1969).

that they were not alike. An attempt to obtain melting points of the compounds by use of a differential scanning calorimeter was unsuccessful since both compounds had dried from PLC solvent extraction as glasses. However, 100 MHz NMR spectra in deuterated benzene showed that although the two compounds were structurally similar, there were differences between them. As seen in Fig. 1, lack of agreement in the aromatic region between 6·0 and 7·0 ppm and in the methoxyl region of 3·0–3·5 ppm positively shows that these are closely related, but not identical, compounds.

This preliminary evidence was substantiated by mass spectral analysis. Conclusive proof of the difference between the two compounds was based on the fragmentation indicated in the Figure involving bond cleavage within the lactone ring of artigenin and its analogue. The lactone ring of the molecular ion of arctigenin fragments to produce a peak at *m/e* 194, ostensibly due to the reaction indicated involving two homolytic bond cleavages. An alternate reaction pathway to *m/e* 194 was eliminated on the basis of exact mass measurement which showed the elemental composition of this peak to by $C_{10}H_{10}O_4$.

In the mass spectrum of the methyl derivative of the matairesinol monoglucoside aglycone, the 194 peak of composition of $C_{10}H_{10}O_4$ is of very low abundance ($<$ 2% relative abundance) but a new peak appears at *m/e* 208 (22 % relative abundance) having the composition $C_{11}H_{12}O_4$. Such an ion is consistent with structure (IV), but not with the alternate possible aglycone. Other peaks in the mass spectra of the two aglycones differed by less than a few per cent relative abundance.

Thus, the structure of the compound resulting from the methylation and hydrolysis of matairesinol monoglucoside (IV) is not identical to artigenin and therefore the structure of matairesinol monoglucoside is as shown (V).

EXPERIMENTAL

Acid Hydrolysis of Arctiin

A *20* mg sample of arctiin was hydrolyzed with 2 ml 0·5 N HCl for 30 min at 100” in an evacuated sealed tube. The aglycone was extracted from the acid mixture with $CHCl_3$ and applied to a preparative SiO_2 plate for development with benzene–EtOH (92: 8). The aglycone band was located under u.v. light, extracted from the SiO_2 with $CHCl_3$ and dried.

Methylation of Matairesinol Monoglucoside

A *50* mg sample of matairesinol monoglucoside was dissolved in 4·8 ml of dried DMF and 1·2 ml CH_3I and 200 mg freshly prepared Ag_2O was added. The mixture was shaken in the dark for 24 hr. An additional 1·0 ml of DMF, 0·4 ml CH_3I and 50 mg Ag_2O was added and shaking continued 66 hr longer. At that time a third similar addition of DMF, CH_3I and Ag_2O was made and shaking continued for 24 hr.

The methylated product was isolated by the addition of $CHCl_3$ to the mixture. The resulting precipitate was washed with $CHCl_3$ and the combined $CHCl_3$ solutions were washed with an aq. KCN solution (2 g KCN-200 ml H_2O). After washing the $CHCl_3$ solution with H_2O, it was dried over $MgSO_4$ and filtered. The residue after solvent removal was a yellow oil.

Acid Hydrolysis of Methylated Matairesinol Monoglucoside

The methylated product was hydrolyzed with 2 ml 1 N ethanolic HCl in an evacuated sealed tube for 90 min at 100”. The entire mixture was applied to a preparative SiO_2 plate and developed with ethyl acetate. The arctigenin analogue band was located under u.v. light, extracted from the SiO_2 with $CHCl_3$ and dried. Since this preparation showed traces of unreacted matairesinol, it was re-applied to a preparative SiO_2 plate and developed with benzene–EtOH (92: 8). Extraction of the relevant band with $CHCl_3$ yielded a pure product.

Instrumentation

Mass spectra were obtained on a Consolidated Electrodynamics 21-110 Mass Spectrometer using the direct introduction probe at 145”. A modified Varian HR 100 was used for the NMR spectra.

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