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AN URUSHIOL DERIVATIVE FROM POISON SUMAC

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Key Word Index—*Toxicodendron vernix*, Anacardiaceae, urushiol derivative, catechols

Abstract—GC analysis of the ethanolic extract of poison sumac (*Toxicodendron vernix*) showed five urushiol components four of which were identical with those from poison ivy (*T radicans*) The new component was determined to be 3-*n*-pentadec-8,11,13-trienylcatechol

INTRODUCTION

In a previous publication, the analysis of the different components of poison ivy (*Toxicodendron radicans*) and poison oak (*T diversilobum*) urushiols were reported [1] The third most widely distributed member of the contact dermatitis causing plants of the family Anacardiaceae is poison sumac (*T vernix*) whose urushiol has not been fully examined and is reported here

RESULTS AND DISCUSSION

GC analysis of poison sumac (*Toxicodendron vernix*) urushiol showed that four of its components were identical with those of poison ivy urushiol and represent 40% of the total The remaining 60% was a single unidentified component GC/MS analysis of the TMSi derivative showed that the new component had the same MW as the triolefinic isomer of poison ivy urushiol and catalytic hydrogenation gave a single product, 3-*n*-pentadecylcatechol (PDC) This indicated that the new component must be a double bond isomer of the 8,11,14-triene component of poison ivy urushiol

The mixture was separated by reversed phase HPLC GC analysis of the separated components showed that the new triene was contaminated with 10% of the 8,11,14-triene The two isomers were only separable by GC and thus the mixture was used for spectral analysis without further purification The presence of a vinyl methyl and the absence of a terminal methylene signal in ^{1}H NMR and ^{13}C NMR of the new triene fixed the position of the terminal double bond at C-13 Osmium tetroxide–potassium periodate oxidation of the dimethyl ethers of the triene mixture gave ω-(2,3-dimethoxyphenyl)-capryl aldehyde Isolation of this aldehyde indicated that the first double bond in the new triene was at C-8 The position of the middle double bond was determined by subjecting the dimethyl ether of the triene mixture and that of pure 8,11,14 triene to osmium tetroxide oxidation, the product of each reaction was then partially oxidized with potassium periodate. GC/MS analysis indicated that two peaks are produced, the first due to ω-(2,3-dimethoxyphenyl)-capryl aldehyde and the second showed ions at m/z 337, 320 and 302 in both cases The presence of identical mass spectral fragments in the partial oxidation reaction products of both trienes indicated that the position of the middle double bond is the same in both compounds This confirms the structure of the new poison sumac component to be 3-*n*-pentadec-8,11,13-trienylcatechol The same triolefinic component has been reported from Japanese Lac urushiol by Sunthankar and Dawson [4], but the assignment of the second and third double bonds was not unequivocal The allergenicity of poison sumac urushiol was found to be similar to that of poison ivy urushiol and the same product could be used for production of tolerance and desensitization to both urushiols [5]

EXPERIMENTAL

Plant material Poison sumac [*T vernix* L (Kuntze)] was collected in May 1978 near Hattiesburg, Mississippi and used immediately after collection The plant was authenticated by Professors Maynard Quimby and Thomas M Pullen and herbarium specimens are stored in the Drug Plant Herbarium, Department of Pharmacognosy, School of Pharmacy, University of Mississippi

General procedures Mps are uncorr. ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz instrument ^{13}C NMR spectra were obtained on a JEOL NJM-FX-60 Fourier transform instrument Chemical shifts were measured in δ-values (ppm) with TMS as int standard $CDCl_3$ was used as solvent in all cases A Finnigan 3200 GC/MS/DS instrument was used for GC/MS analysis at 70 eV The TMSi derivatives were prepared using BSTFA–pyridine and chromatographed using a 3% OV-225 column at 210° A Beckman GC-65 instrument was used for the GC analysis following lit procedures [2]

A Waters Associates Prep LC/system 500A liquid chromatograph with Prep PAK-500/C_{18} cartridge and RI detector was used for preparative separations For analytical studies, a Waters Associates chromatograph, equipped with U6K injector, a model 6000 pump and a model 440 UV detector at 254 nm, was used A 30 cm × 3 9 mm i d reversed phase column (μBondapak C_{18}) with a 10 μm particle size was used and analysis was done as previously reported [3]

Extraction Poison sumac (*T vernix*) leaves (141 5 g) were extracted by percolation with 95% EtOH (2 l × 6) at room temp After removal of the solvent, 28 5 g of residue was obtained Purification and other procedures have been described earlier [1–5]

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ACETYLENIC COMPOUNDS FROM *BIDENS GRAVEOLENS**

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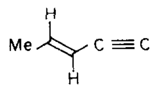
Key Word Index—*Bidens graveolens*, *Bidens* sp., Compositae; acetylenic compounds, C_{14}-acetylene, C_{17}-acetylene, monoterpene.

Abstract—*Bidens graveolens* afforded, in addition to known compounds, two new acetylenic esters and a monoterpene diol Other species only gave known compounds.

The roots of *Bidens graveolens* Mart. afforded germacrene D, bicyclogermacrene, cinnamyl alcohol and its acetate, **1a** [1], **2** [1] and **10** as well as the keto ester, **6**, the structure of which followed from its UV spectrum, molecular formula and ^{1}H NMR spectral data (Table 1). The presence of an isobutyrate group was deduced from the typical ^{1}H NMR signals, while the positions and the stereochemistry of the double bonds and the position of the keto group followed from spin decouplings, which clearly showed the sequences **A** and **B**.

As the UV spectrum required the presence of an enediynene chromophore [2], the structure of **6** was settled. The aerial parts afforded germacrene D, bicyclogermacrene, spathulenol, caryophylleneepoxide (**3**), the hydroxy germacradiene, **4**, the diynenes, **7** and **8** [2], as well as the isobutyrate, **9**, the structure of which followed from its ^{1}H NMR spectrum (Table 1), which was close to that of the known acetate [2]. Again, the nature of the ester group followed from the typical ^{1}H NMR signals. Furthermore, a small amount of **5a** was isolated. The



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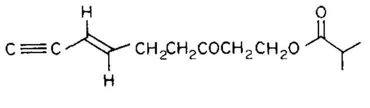

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*Part 262 in the series "Polyacetylenic Compounds". For Part 261 see Greger, H, Grenz, M and Bohlmann, F (1982) *Phytochemistry* **21**, 1071