Phytochemistry, 1978, Vol 17, pp 1435–1436 ©Pergamon Press Ltd Printed in England. 0031-9422/78/0801-1435 $02.00/0

TERPENE HYDROCARBONS FROM *PSIDIUM GUAJAVA*

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(*Received* 5 *January* 1978)

Key Word Index—*Psidium guajava*; Myrtaceae; guava; essential oils; sesquiterpenes; curcumene.

Abstract—An extract of whole guava puree, after TLC and GLC, showed the presence of two monoterpenes and nine sesquiterpenes. β-Caryophyllene comprised 95% of this fraction. Possible significance of these hydrocarbons to natural insect attractants and to guava aroma is noted.

INTRODUCTION

The common guava (*Psidium guajava* L.) is a subtropical fruit that is found in the United States in central and southern Florida and in Hawaii. In these areas, the guava has become a weed tree or shrub. and much of the fruit is harvested from wild or semi-wild plants [1]. Guavas can be consumed as fresh fruit, but they are more frequently used commercially in jams, jellies and mixed tropical fruit juice drinks. Guavas are also a preferred host plant for the Caribbean fruit fly (*Anastrepha suspensa*) and they are seldom found in the ripe state in Florida without larvae of the fly present [2].

Even though guavas are consumed in a variety of food products, the chemicals responsible for the flavour and aroma of guava fruit have received relatively little attention. Misra and Seshadri [3] measured the levels of several polyphenols in guava fruit at different stages of maturity. Smith and Siwatibau [4] identified several sesquiterpene hydrocarbons and alcohols in guava leaves and correlated their presence with varietal differences. Stevens *et al.* [5] identified 22 components of a volatile fraction from guava puree, including two terpenes.

We report the identification of 11 terpenes from guava and their possible significance of flavour and insect attractant properties of guava fruit.

RESULTS AND DISCUSSION

The hydrocarbons separated from guava puree (Table 1) were identified by comparison of GLC R_ts and MS and/or IR spectra with those for authentic samples. Of the 11 hydrocarbons listed, only two, limonene and β-caryophyllene, had been identified previously in guava fruit [5]. In our hydrocarbon fraction, these two compounds comprised over 95% of the total hydrocarbons present, and β-caryophyllene was by far the largest single component. Other hydrocarbons identified include one monoterpene, β-pinene, and eight sesquiterpenes. Two of the sesquiterpenes, β-copaene and β-bisabolene, were present in greater quantity than that of (+)-limonene.

All these hydrocarbons have been found previously in other foods. Thus, all compounds except β-selinene and curcumene were reported in citrus essential oils [6].

Table 1. Hydrocarbons from guava puree extract

Hydrocarbon	Estimated* percentage	Identified by† R_t	IR	MS
β-Pinene	<0.5	×		×
Limonene	0.5	×	×	×
β-Copaene	1.0	×	×	×
β-Caryophyllene	95.0	×	×	×
Farnesene	<0.5	×	×	×
α- and β-Humulene	0.5	×	×	×
β-Bisabolene	1.0	×	×	×
α-Selinene	<0.5	×	×	
β-Selinene	<0.5	×	×	
Δ-Cadinene	<0.5	×	×	
Curcumene	<0.5		×	

* Based on relative GLC areas of components in TLC fraction 1.

† Comparison with authentic compound.

β-Selinene was identified as present in celery essential oil [7], and curcumene as present in cinnamon and other spices [8]; but neither had been reported as a constituent of fruits or their essential oils. However, β-selinene was found in leaf oil from wild guavas by Smith and Siwatibau [4], so its presence in guava fruit was not surprising. In this study on the leaf oils [4], four sesquiterpenes were also identified. Only two of these, caryophyllene and β-bisabolene, were found in our work. Smith and Siwatibau [4] found that caryophyllene was consistently present in leaf oils from all three chemotypes studied, but that the presence of the other sesquiterpenes depended on the chemotype. Caryophyllene was not always the major sesquiterpene present in their leaf oil extracts.

The whole guava extract and the hydrocarbon fraction were screened for ability to stimulate ovaposition by the Caribbean fruit fly. Although whole extract was stimulatory, the hydrocarbon fraction was not [2]. Several of the hydrocarbons identified are known attractants for other insects [9, 10], and the possibility exists that certain of these hydrocarbons do attract the Caribbean fruit fly even though none induced oviposition as tested. Details of the insect behaviour studies involving guava extracts will be published elsewhere [2].

Guava aroma is highly desirable in processed products such as jellies and blended fruit drinks. Unlike our total guava extract the hydrocarbon fraction was devoid of fresh guava aroma. However, Shaw [6] has shown with certain essential oils that when a single hydrocarbon component is by far the major constituent, it can exert a profound influence on flavour in combination with minor oxygenated components. Therefore, caryophyllene might yet be shown to be important in guava aroma.

EXPERIMENTAL

Extraction methods. Wild Florida guavas (*Psidium guajava* L.) were used. *Ca* 100 kg of whole fruit was pureed in a Chisholm Ryder (Chisholm Ryder C., Inc., Niagra Falls, NY) finisher (5.1 mm screen) at 15 psi air pressure. The puree, about 75 kg, was placed in a cold walled stainless steel tank held at −1° and mixed with 19 l. CH_2Cl_2. The organic layer was allowed to settle to the bottom and removed through a valve; it was then concd in a rotary evporator at room temp. to afford 58 g dark brown residue (total extract) with a strong aroma characteristic of fresh guava.

TLC separation. The total extract, not readily separable by GLC because of its viscosity, was separated into 4 fractions by PLC on Si gel HF_{254} plates 1 mm thick, with hexane–Me_2CO (49:1). The least polar fraction, which contained the terpenes and sesquiterpenes, by far the largest of the 4 fractions, was removed, then eluted with developing solvent. The eluate was concd and then analysed by GC–MS and IR spectroscopy.

GC–MS analyses. The gas chromatograph used for GC–MS analyses was a Varian Model 1400 instrument equipped with a flame ionization detector and a 1:1 splitter. Injection port and detector temperature was 225°. A 0.76 mm × 305 m column coated with Carbowax 20 M was programmed from 70 to 200° at 1°/min with an He flow rate of 10 ml/min. GC–MS separations were obtained with a Bell & Howell Model 21-490 mass spectrometer at 70 eV coupled through a jet separator to GC

IR analyses. Separations for IR analyses were made by an F&M Model 700 gas chromatograph equipped with 5.1 mm × 6.1 m stainless steel columns packed with 40% Carbowax 20 M on 60–80 mesh Gas Chrom P. The thermal conductivity detector and injection port temps were 275 and 245°, respectively. Temp. was programmed from 100 to 220° at 1°/min at a He flow rate of 100 ml/min. IR spectra were determined as thin-liquid films.

REFERENCES

1. Bailey, L. H. and Bailey, E. Z. (1976) *Hortus Third* p. 527. Macmillan, New York.
2. Greany, P., private communication.
3. Misra, K. and Seshadri, T. R. (1965) *Phytochemistry* **7**, 641.
4. Smith, R. M. and Siwatibau, S. (1975) *Phytochemistry* **14**, 2013.
5. Stevens, K. L., Brekke, J. E. and Stern, D J. (1970) *J. Agric. Food Chem.* **18**, 598.
6. Shaw, P. E. (1977) in *Citrus Science and Technology* (Nagy, S., Shaw, P. E. and Veldhuis, M. K. eds) Vol. 1, p. 427. Avi, New York.
7. Wilson, C. W. (1969) *J. Food Sci.* **34**, 521.
8. Asakawa, Y., Komatsu, T., Hayashi, S. and Matsurra, T. (1971) *Flavour Ind.* **2**, 114.
9. Sutherland, O B. and Hutchins, R. F. N. (1972) *Nature* **23**, 1970.
10. Jacobson, M. (1972) *Insect Sex Pheromones* p. 251. Academic Press, New York.

Phytochemistry, 1978, Vol 17, pp 1436–1437 ©Pergamon Press Ltd Printed in England 0031-9422/78/0801-1436 $02 00/0

TWO MINOR DITERPENES FROM *EUPHORBIA* LATEX

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(*Received* 24 *January* 1978)

Key Word Index—*Euphorbia poisonii*; Euphorbiaceae; diterpenes; 20-*O*-acetyl-resiniferonol-9,13,14-*ortho*phenylacetate; 12-deoxyphorbol-13-O-[p-acetoxyphenylacetate]-20-acetate.

The section *Euphorbium* of the genus *Euphorbia* consists of succulent species indigenous to central and southern Africa. From the latex of several species of *Euphorbium* several novel ester diterpenes have been obtained [1–6]. *Euphorbia poisonii* is a member of the section *Euphorbium* from which esters of 12-deoxyphorbol, 12-deoxy-16-hydroxy-phorbol and resiniferonol have previously been isolated [7–9]. Further examination of the Et_2O fraction of the latex extract by means of both column chromatography and TLC yielded two new minor diterpene esters **1** and **3** in an impure form.

20-0-*Acetyl-resiniferonol*-9,13,14-ortho *phenylacetate* **1**

This ester was purified by partition TLC. Kieselguhr G plates (0.5 mm) were developed for 20 cm in 20% dipropylene glycol in Me_2CO and then air dried. The coated plates were developed twice in *n*-heptane–C_6H_6 9:1 (hR_f 32). After recovery of the ester [10], it was again purified by a second partition TLC step as before using *n*-heptane–benzene 17:3 (hR_f 51) as solvent and developing twice. The recovered resin produced a single black-orange spot on analytical TLC after spraying with 50% aq H_2SO_4 and heating. This compound was