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# Oxygenated monoterpenoids from badea (*Passiflora quadrangularis*) fruit pulp

Coralia Osorio[a], Carmenza Duque[a,*], Yoshinori Fujimoto[b]

[a]*Departamento de Química, Universidad Nacional de Colombia, AA 14490, Bogotá, Colombia*
[b]*Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan*

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## Abstract

The new monoterpenoids (2*E*)-2,6-dimethyl-2,5-heptadienoic acid, (2*E*)-2,6-dimethyl-2,5-heptadienoic acid β-D-glucopyranosyl ester, (5*E*)-2,6-dimethyl-5,7-octadiene-2,3-diol, and (3*E*)-3,7-dimethyl-3-octene-1,2,6,7-tetrol were isolated from the fruit pulp of *Passiflora quadrangularis* along with the known 2,5-dimethyl-4-hydroxy-3(2H)-furanone β-D-glucopyranoside. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* *Passiflora quadrangularis*; Passifloraceae; 2,6-dimethyl-2,5-heptadienoic acid; 2,6-dimethyl-2,5-heptadienoic acid β-D-glucopyranosyl ester; 2,6-dimethyl-5,7-octadiene-2,3-diol; 3,7-dimethyl-3-octene-1,2,6,7-tetrol

## 1. Introduction

*Passiflora quadrangularis* L. (badea) is a wild vine relatively abundant in some regions of tropical America. Its oblong fruit (length 30 cm, width 12 cm, approx.) has a slightly acidic pulp with a pleasant and refreshing aroma, which is used locally to prepare different kinds of soft drinks. Despite its popularity among the consumers, as far as we know there are no published studies in the literature on the chemical composition of this fruit, and only one report on the isolation of a triterpene glycoside from the leaves of the plant (Orsini, Pelizzoni & Verotta, 1986). To continue our studies on flavour chemistry of Colombian fruits, we performed a preliminary screening of volatiles isolated from the pulp, finding a high amount of two oxygenated monoterpenoids whose odour strongly resembles to the aroma of the fresh fruit (Osorio, Duque, Suarez, Salamanca & Uruena, submitted). Additionally, we examined the methanolic extract obtained from the pulp, searching for other flavour-related compounds. We report in this paper the isolation and structure elucidation of four new monoterpenoids (2*E*)-2,6-dimethyl-2,5-heptadienoic acid (**1**), its β-D-glucopyranosyl ester (**2**), (5*E*)-2,6-dimethyl-5,7-octadiene-2,3-diol (**3**) and (3*E*)-3,7-dimethyl-3-octene-1,2,6,7-tetrol (**4**) together with the known β-D-glucopyranoside of 2,5-dimethyl-4-hydroxy-3(2H)-furanone (Roscher, Herderich, Steffen, Schreier & Schwab, 1996).

## 2. Results and discussion

The two major volatiles present in the pentane–dichloromethane extract obtained by liquid–liquid extraction of the *P. quadrangularis* fruit pulp were purified over silica gel to afford pure compounds **1** and **3**. Furthermore, the methanolic extract of the same fruit pre-separated by MLCCC was fractionated on silica gel to give compounds **2** and **4**, and the β-D-glucopyranoside of 2,5-dimethyl-4-hydroxy-3(2H)-furanone (Furaneol®).

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* Corresponding author Tel.: +57-1-316500 ext. 14472; fax: +57-1-3165220.

*E-mail address:* cduqueb@ciencias.ciencias.unal.edu.co (C. Duque).

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Table 1
$^1$H- and $^{13}$C-NMR spectral data for compounds **1**, **2** and **2a**

| Atom No | **1**[a] | | **2**[b] | | **2a**[a] |
|---|---|---|---|---|---|
| | $^1$H | $^{13}$C | $^1$H | $^{13}$C | $^1$H |
| 1 | – | 173.5 | – | 168.2 | – |
| 2 | – | 126.6 | – | 127.7 | – |
| 3 | 6.86 (*tq*, 7.6, 1.5) | 143.7 | 6.83 (*tq*, 7.6, 1.5) | 144.1 | 6.81 (*tq*, 7.6, 1.5) |
| 4 | 2.89 (*t*, 7.2) | 28.0 | 2.91 (*t*, 7.6) | 28.8 | 2.87 (*t*, 7.6) |
| 5 | 5.12 (*br t*, 7.3, 1.5) | 119.8 | 5.13 (*m*) | 121.0 | 5.10 (*m*) |
| 6 | – | 133.9 | – | 134.8 | – |
| 7 | 1.65 (*br s*) | 25.6 | 1.66 (*s*) | 25.8 | 1.64 (*s*) |
| 8 | 1.86 (*br s*) | 12.0 | 1.87 (*s*) | 12.4 | 1.85 (*s*) |
| 9 | 1.71 (*br s*) | 17.6 | 1.71 (*s*) | 17.9 | 1.71 (*s*) |
| 1′ | | | 5.52 (*d*, 7.8) | 95.9 | 5.75 (*d*, 7.8) |
| 2′ | | | 3.28–3.43 (*m*) | 74.0 | 5.22 (*t*, 8.5) |
| 3′ | | | 3.28–3.43 (*m*) | 78.1 | 5.28 (*t*, 9.3) |
| 4′ | | | 3.28–3.43 (*m*) | 70.9 | 5.15 (*t*, 10.0) |
| 5′ | | | 3.28–3.43 (*m*) | 78.7 | 3.87 (*ddd*, 10.0, 4.4, 2.2) |
| 6′ | | | 3.83 (*dd*, 12.0, 1.7)<br>3.67 (*dd*, 12.0, 4.4) | 64.3 | 4.11 (*dd*, 12.4, 2.2)<br>4.30 (*dd*, 12.4, 4.4) |
| Ac | | | | | 2.01, 2.02, 2.04, 2.09 (*s*) |

[a] In $CDCl_3$.
[b] In $CD_3OD$.

Compound **1**, $C_9H_{14}O_2$, exhibited an $[M]^+$ ion at *m/z* 154 in the EIMS spectrum. The $^1$H-NMR spectrum (Table 1) of **1** showed signals for three broad singlet methyls ($\delta$ 1.65, 1.86 and 1.71), one methylene [$\delta$ 2.89 ($t, J = 7.2$ Hz)] and two olefinic protons [$\delta$ 5.12 ($brt, J = 7.3$, 1.5 Hz) and 6.86 ($tq, J = 7.6$, 1.5 Hz)]. $^1$H-NMR decoupling experiments clearly showed correlations between the methylene group and the two olefinic protons. The $^{13}$C-NMR spectrum of **1** (Table 1) showed signals of a carboxy carbon ($\delta$ 173.5), four olefinic carbons ($\delta$ 119.8, 126.6, 133.9 and 143.7), along with four aliphatic carbons. On the basis of these results, the structure of **1** was determined as (2*E*)-2,6-dimethyl-2,5-heptadienoic acid. (*E*)-Geometry of the C-2 double bond was obvious from upfield chemical shifts of the methyl group at C-2 ($\delta_H$ 1.86, $\delta_C$ 12.0).

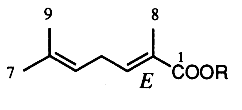
Compound **2**, $C_{15}H_{24}O_7$, showed $[M + H]^+$ ion peak at *m/z* 317 in the FABMS spectrum. The $^1$H- and $^{13}$C-NMR spectral data (Table 1) of **1** and **2** resembled each other except for the presence of resonances of a hexose moiety in **2**. The (*E*)-geometry of the C-2 double bond was confirmed by an NOE experiment in which irradiation of the methyl group at $\delta$ 1.87 enhanced the signal intensity of the methylene group at $\delta$ 2.91. The hexose moiety was readily identified as glucose based on analysis of the $^1$H-NMR spectral data (Table 1) of the tetraacetate derivate **2a**. The anomeric proton signal at $\delta$ 5.52 ($d, J = 7.8$ Hz) of **2a** also suggested a β-glucosidic ester linkage. On the basis of these data, compound **2** was established to be the β-D-glucopyranosyl ester of **1**.

Compound **3**, $C_{10}H_{18}O_2$, showed a $[M + H]^+$ ion peak at *m/z* 171 in the CIMS spectrum. The $^1$H-NMR spectrum (Table 2) exhibited signals of three singlet methyls at $\delta$ 1.21, 1.25 and 1.78, one aliphatic methylene at $\delta$ 2.29–2.35 (*m*), one oxymethine at $\delta$ 3.47 ($dd, J = 9.5$, 3.4 Hz), one vinyl group at $\delta$ 4.99 ($d, J = 10.7$ Hz), 5.14 ($d, J = 17.3$ Hz) and 6.41 ($dd, J = 17.2$, 10.7 Hz), and one olefinic methine at $\delta$ 5.59 ($t, J = 7.3$ Hz). The methylene protons were found to be spin–spin coupled to the oxymethine and the olefinic methine protons by decoupling experiments. The $^{13}$C-NMR spectrum (Table 2) of **3** exhibited signals for four ali-

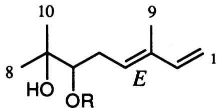
Table 2
$^1$H- and $^{13}$C-NMR spectral data for compounds **3** and **4**

| Atom No | **3**[a] | | **4**[b] | |
|---|---|---|---|---|
| | $^1$H | $^{13}$C | $^1$H | $^{13}$C |
| 1 | 4.99 (*d*, 10.7)<br>5.14 (*d*, 17.3) | 111.6 | 3.49 (*dd*, 11.0, 5.8)<br>3.54 (*dd*, 11.0, 5.4) | 65.6/65.7 |
| 2 | 6.41 (*dd*, 17.3, 10.7) | 141.1 | 4.03 (*t*, 6.1) | 78.9/79.0 |
| 3 | – | 136.9 | – | 137.2/137.2 |
| 4 | 5.59 (*t*, 7.3) | 128.9 | 5.60 (*t*, 7.0) | 126.3/126.4 |
| 5 | 2.29–2.35 (*m*) | 30.9 | 2.07 (*m*)<br>2.38 (*m*) | 30.8/30.9 |
| 6 | 3.47 (*dd*, 9.5, 3.4) | 77.9 | 3.30 (*m*) | 79.6 |
| 7 | – | 72.8 | – | 73.7/73.7 |
| 8 | 1.21 (*s*) | 23.6 | 1.15 (*s*) | 24.8/24.8 |
| 9 | 1.78 (*s*) | 12.0 | 1.63 (*s*) | 12.4/12.5 |
| 10 | 1.25 (*s*) | 26.5 | 1.18 (*s*) | 25.9/25.9 |

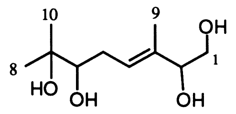
[a] In $CDCl_3$.
[b] In $CD_3OD$.



**1**: R=H
**2**: R=β-D-Glu
**2a**: R=β-D-Glu(OAc)$_4$



**3**: R=H
**3a**: R=(*S*)-MTPA
**3b**: R=(*R*)-MTPA



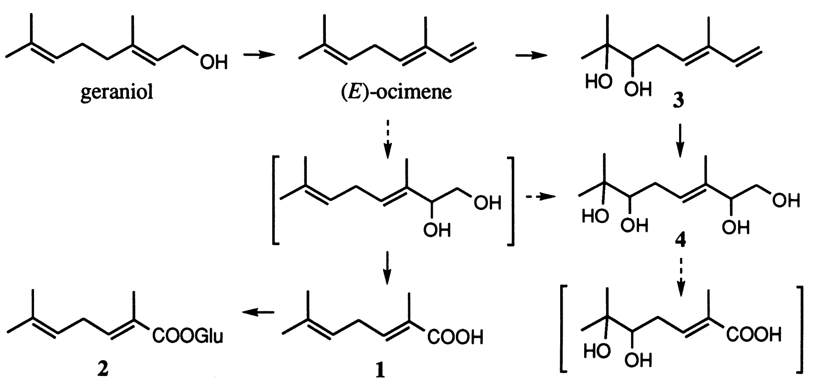
**4**

phatic carbons, two oxymethine carbons ($\delta$ 72.8 and 77.9) and four olefinic carbons ($\delta$ 111.6, 128.9, 136.9 and 141.1). These spectral data indicated compound **3** to be 2,6-dimethyl-5,7-octadiene-2,3-diol (Note that chemical abstract numbering system is different from that of the Structure Insert). Furthermore, NMR data were in good agreement with those published for synthetic (5*E*)-2,6-dimethyl-5,7-octadiene-2,3-diol (Fournier-Nguefack, Lhoste & Sinou, 1997). Isolation of the (5*Z*)-isomer from *Aster bakeranus* (Tsankova & Bohlmann, 1983) was previously reported, and the $^1$H-NMR spectral data of **3** were clearly different from those reported for the *Z*-isomer. Thus, the structure of **3** was established as (5*E*)-2,6-dimethyl-5,7-octadiene-2,3-diol. The absolute stereochemistry at the C-3 position (C-6 in the Structure Insert) was investigated by use of advanced Moshers' ester method (Ohtani, Kusumi, Kashman & Kakisawa, 1991) ($^1$H-NMR data of (*S*)- and (*R*)-MTPA esters (**3a** and **3b**, respectively) are shown in Section 3). This study concluded that compound **3** is a 4:1 mixture of (3*S*)- and (3*R*)-antipodes, respectively.

Compound **4**, $C_{10}H_{20}O_4$, showed a $[M + H]^+$ ion peak at *m*/*z* 205 in the FABMS spectrum. The NMR data of **4** were similar to those of **3**. Significant differences observed in the $^1$H-NMR spectral data are the absence of signals for the vinyl group found in **3**, and the appearance of signals of one oxymethine at $\delta$ 4.03 (*t*, $J = 6.1$ Hz) and one oxymethylene at $\delta$ 3.49 (*dd*, $J = 11.0$, 5.8 Hz) and 3.54 (*dd*, $J = 11.0$, 5.4 Hz) in **4**. The H–H COSY spectrum of **4** revealed the connectivity of the oxymethine and oxymethylene protons. Furthermore, the $^{13}$C-NMR spectrum of **4** supported the presence of a $-CHOH-CH_2OH$ unit ($\delta$ 78.9/79.0 and 65.6/65.7). In an NOE experiment, irradiation of the olefinic methyl at $\delta$ 1.63 enhanced the signal intensity of methylene protons at $\delta$ 3.30. On the basis of these data, the compound **4** was determined as (3*E*)-3,7-dimethyl-3-octene-1,2,6,7-tetrol. Importantly, most of the $^{13}$C-NMR spectroscopic signals (Table 2) of **4**, were observed as pairs of approximately equal intensity, thus indicating a 1:1 diasteroisomeric nature of **4**. Absolute configuration of compound **4** remains to be established.

Finally from the MeOH extract, the known 2,5-dimethyl-4-hydroxy-3(2H)-furanone β-D-glucopyranoside (a 1:1 diasteroisomeric mixture) (Roscher et al., 1996) was isolated and characterized by comparison of its $^1$H- and $^{13}$C-NMR spectral data with those published.

Compounds **1**, **2**, **3** and **4** have been isolated here for the first time from natural sources, although (5*E*)-2,6-dimethyl-5,7-octadiene-2,3-diol (**3**) was previously synthesized. These structures suggest the presence of an oxidative biosynthetic pathway in fruits of *P. quadrangularis*, as shown in Scheme 1. Furthermore, it is interesting to note that an olefinic positional isomer of **4**, 3,7-dimethyl-3(9)-octene-1,2,6,7-tetrol, was also isolated as a diasteroisomeric mixture from the fruit of *Cnidium monnieri* (Umbelliferae) (Kitajima & Tanaka, 1993) and *Foeniculum vulgare* (Umbelliferae) (Ishikawa, Tanaka & Kitajima, 1998). Since it has



Scheme 1. Postulated biogenic correlation. Compounds in parentheses have not been reported.

been found that oxygenated monoterpenoids and their glycoconjugates have roles in the generation of volatile compounds in fruits and wine (Engel & Tressel, 1983; Strauss, Wilson, Gooley & Williams, 1986; Winterhalter, Katzenberger & Schreier, 1986), further study on possible roles of **1**, **2**, **3** and **4** as aroma precursors in *P. quadrangularis* is underway in our laboratory.

## 3. Experimental

### *3.1. General*

$^{1}$H- and $^{13}$C-NMR (400 and 100 MHz, respectively) spectra were acquired on a JEOL lambda-400 spectrometer. NMR spectra recorded in $CDCl_3$ were referenced to TMS signal ($\delta$ 0.0) for $^{1}$H and the solvent signal ($\delta$ 77.0) for $^{13}$C; spectra recorded in $CD_3OD$ were referenced to the solvent signal ($\delta_H$ 3.3 and $\delta_C$ 49.0). FABMS spectra were recorded in glycerol or NBA matrix in the positive ion mode with a JEOL JMS-AX505HA spectrometer. GC–MS (EI–MS, 70 eV) was carried out on a Shimadzu GCMS QP5050 instrument. Chemical ionization mass spectrometry (CIMS) employed a Shimadzu 9020 DF mass spectrometer using isobutane as a reactant gas. For multilayer coil countercurrent chromatography (MLCCC) a multilayer coil extractor–separator, P.C. Inc. Potomac, was used. Optical rotations were measured on a JASCO DIP-360 digital polarimeter.

### *3.2. Plant material*

Ripe *P. quadrangularis* fruits were purchased in a local market of Neiva, Huila, Colombia, in August, 1998.

### *3.3. Isolation of free volatile extract*

Fruit pulp of *P. quadrangularis* (6 kg, from 46 kg of fruits) was blended in a mixer at natural pH (3.5) of the fruit homogenate. After centrifugation (10,000 g, 40 min), the supernatant was extracted with pentane–dichloromethane (1:1) in a continous liquid–liquid extractor for 36 h. The organic extract was dried over $Na_2SO_4$ and concentrated to 2 ml volume in a vigreux column. The concentrated extract was fractionated over silica gel (40 g, 32–63 mm) with the following eluant solutions: pentane–$Et_2O$ (9:1), pentane–$Et_2O$ (2:1), pentane–$Et_2O$ (1:1), pentane–$Et_2O$ (1:2) and $Et_2O$ to obtain five fractions, fr I to fr V, respectively. Fr III and fr V were further fractionated by chromatography over silica gel using hexane–AcOEt (7:1 → 4:1) as eluents to yield **1** (9 mg) and **3** (6 mg), respectively.

### *3.4. Isolation of polar extract*

Fruit pulp of *P. quadrangularis* (7.4 kg, from 42 kg of fruits) was blended in a mixer with the pH adjusted to 7.0 with 5 N NaOH. After centrifugation (10,000 g, 30 min), the supernatant was subjected to XAD-2 column chromatography (Gunata, Bayonove, Baumes & Cordonnier, 1985). The column was rinsed with water and then eluted with MeOH. The MeOH eluate afforded a crude extract (4.2 g), which was fractionated by MLCCC (75 m × 2.6 mm i.d. PTFE tubing; total volume 400 ml) in portions of 1.5 g. The MLCCC apparatus was operated at 800 rpm, using $CHCl_3$–MeOH–$H_2O$ (7:13:8) as the solvent system with the less dense layer as the mobile phase at 1 ml/min. Fifty fractions of 10 ml were collected in each separation. Combined fractions 20–30 were concentrated under vaccum to afford dry residue (381 mg), which was repeatedly chromatographed over silica gel with $CHCl_3$–MeOH (7:1), $CHCl_3$–MeOH (5:1), $CHCl_3$–MeOH (4:1) and $CHCl_3$–MeOH (3:1) as eluents. Elution with $CHCl_3$–MeOH (7:1) afforded **2** (18 mg). The fraction obtained by elution with $CHCl_3$–MeOH (5:1) was finally fractionated over silica gel, using the less dense layer of system AcOEt–BuOH–$H_2O$ (8:2:5) as eluent; combined 9–10 and 15–19 gave **4** (25 mg) and furaneol β-D-glucopyranoside (20 mg) as an oil, respectively.

### *3.5. (2E)-2,6-dimethyl-2,5-heptadienoic acid (**1**)*

Colorless oil. CIMS *m*/*z*: 155 $[M + H]^+$; GC-MS *m*/*z* (rel. int.): 154 $[M]^+$ (10), 139 (2), 136 (2), 125 (9), 121 (4), 111 (100), 109 (35), 98 (35), 93 (30), 91 (20), 81 (18), 79 (16), 77 (19), 69 (12), 67 (40), 65 (11), 57 (5), 55 (30), 53 (22), 51 (10), 45 (16), 43 (48), 41 (55), 39 (48). $^{1}$H- and $^{13}$C-NMR spectral data: Table 1.

### *3.6. (2E)-2,6-dimethyl-2,5-heptadienoic acid β-D-glucopyranosyl ester (**2**)*

Colorless oil. $[\alpha]_D^{25}$ + 12.6° (MeOH; *c* 0.78); FABMS *m*/*z*: 339 $[M + Na]^+$, 317 $[M + H]^+$, 299 $[M + H\text{–}H_2O]^+$, 155 $[M + H\text{–glucosyl}]^+$. HR-FABMS Found 317.1634 $[MH]^+$, $C_{15}H_{25}O_7$ requires 317.1600. $^{1}$H- and $^{13}$C-NMR spectral data: Table 1.

### *3.7. (2E)-2,6-dimethyl-2,5-heptadienoic acid β-D-glucopyranosyl ester tetraacetate (**2a**)*

Acetylation of compound **2** (3 mg) in the usual manner ($Ac_2O$–Py) gave compound **2a** (3 mg) as an oil. FABMS failed to show the expected quasi molecular ion but a very intense ion was observed at *m*/*z*: 331. $^{1}$H-NMR spectral data: Table 1.

Table 3
$^1$H-NMR spectral data for compounds **3a** and **3b**

| Position | **3a** | **3b** | $\Delta\delta_{S\text{-}R}$ |
|---|---|---|---|
| 1-$H_a$ | 4.97 (*d*, 10.7) | 5.01 (*d*, 10.7) | −0.04 |
| 1-$H_b$ | 5.09 (*d*, 17.6) | 5.15 (*d*, 17.6) | −0.06 |
| 2-H | 6.28 (*dd*, 17.3, 10.8) | 6.35 (*dd*, 17.4, 10.7) | −0.07 |
| 9-Me | 1.66 (*s*) | 1.73 (*s*) | −0.07 |
| 4-H | 5.37 (*t*, 7.2) | 5.49 (*t*, 7.4) | −0.12 |
| 5-$H_2$ | 2.49 (*m*) | 2.56 (*m*) | −0.08 |
| 8-Me | 1.27 (*s*) | 1.21 (*s*) | +0.06 |
| 10-$H_3$ | 1.24 (*s*) | 1.19 (*s*) | +0.05 |
| MeO | 3.49 (*s*) | 3.52 (*s*) | |
| Ph | 7.35–7.57 (*m*) | 7.34–7.58 (*m*) | |

### *3.8. (3S)-(5E)-2,6-dimethyl-5,7-octadiene-2,3-diol (**3**)*

Colorless oil. $[\alpha]_D^{23} - 19.7°$ ($CH_2Cl_2$, *c* 0.62); CIMS *m/z*: 171 $[M + H]^+$; GC–MS *m/z* (rel. int.): 170 $[M]^+$ (5), 152 (13), 137 (3), 119 (1), 109 (12), 91 (8), 89 (12), 83 (11), 82 (62), 81 (53), 79 (29), 77 (10), 71 (32), 68 (20), 67 (54), 59 (86), 57 (8), 55 (22), 53 (17), 51 (5), 45 (7), 43 (100), 41 (70), 39 (35). $^1$H- and $^{13}$C-NMR spectral data: Table 2.

### *3.9. (S)- and (R)-MTPA esters of compound **3***

Compounds **3a** and **3b** were prepared from **3** by treatment with (*R*)-MTPACl and (*S*)-MTPACl, respectively, in pyridine. The $^1$H-NMR data ($CDCl_3$) of **3a** and **3b** and $\Delta\delta_{S\text{-}R}$ values are listed in Table 3. The spectra showed signals of the both compounds in ca. 1:4 intensity.

### *3.10. (3E)-3,7-dimethyl-3-octene-1,2,6,7-tetrol (**4**)*

Colorless oil. $[\alpha]_D^{25} - 11.9°$ (MeOH, *c* 0.67); FABMS *m/z*: 227 $[M + Na]^+$, 205 $[M + H]^+$, 187 $[M + H–H_2O]^+$, 169 $[M + H–2H_2O]^+$. HR-FABMS Found 205.1417 $[M + H]^+$, $C_{10}H_{21}O_4$ requires 205.1440. $^1$H- and $^{13}$C-NMR spectral data: Table 2.

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## References

Engel, K-. H., & Tressl, R. (1983). *J. Agric. Food Chem*, *31*, 998.

Fournier-Nguefack, C., Lhoste, P., & Sinou, D. (1997). *Tetrahedron*, *53*, 4353.

Gunata, Y. Z., Bayonove, C. L., Baumes, R. L., & Cordonnier, R. E. (1985). *J. Chromatogr*, *331*, 83.

Ishikawa, T., Tanaka, Y., & Kitajima, J. (1998). *Chem. Pharm. Bull*, *46*, 1748.

Kitajima, J., & Tanaka, Y. (1993). *Chem. Pharm. Bull*, *41*, 1667.

Ohtani, I., Kusumi, T., Kashman, Y., & Kakisawa, H. (1991). *J. Am. Chem. Soc*, *113*, 4092.

Orsini, F., Pelizzoni, F., & Verotta, L. (1986). *Phytochemistry*, *25*, 191.

Osorio, C., Duque, C., Suarez, M., Salamanca, L. E., & Uruena, F. *J. High Resol. Chromatogr*., submitted.

Roscher, R., Herderich, M., Steffen, J-. P., Schreier, P., & Schwab, W. (1996). *Phytochemistry*, *43*, 155.

Strauss, C. R., Wilson, B., Gooley, P. R., & Williams, P. J. (1986). In T. H. Parliment, & R. Croteau, *Biogeneration of Aromas* (p. 222). In *ACS Symposium Series*, *317*. Washington DC: American Chemical Society.

Tsankova, E., & Bohlmann, F. (1983). *Phytochemistry*, *22*, 1285.

Winterhalter, P., Katzenberger, D., & Schreier, P. (1986). *Phytochemistry*, *25*, 1347.