

New Constituents Related to 3-Methyl-2,4-nonanedione Identified in Green Tea

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The volatile constituents of two exquisite green tea varieties, Kiyosawa tea from Japan and Long Jing tea from China, were investigated in order to identify new compounds responsible for the characteristic flavor of a green tea brew. The extracts were prepared by solid-phase extraction using Oasis-HLB-cartridges. Besides the common compounds of green tea chemistry, the already described compounds 3-methyl-2,4-nonanedione (**1**) and 3-hydroxy-3-methyl-2,4-nonanedione (**2**), products of degradation of furan fatty acids, as well as three new compounds related to compound **1** were identified. These were 1-methyl-2-oxopropyl hexanoate (**3**), 1-methyl-2-oxoheptyl acetate (**4**) and 2-butyl-4,5-dimethyl-3(2*H*)-furanone (**5**). Their syntheses and spectroscopic data are reported. Compound **2** increases the sweet, creamy aroma and the characteristic mouthfeel of a green tea flavor, compounds **3** and **4** contribute to its floral, juicy notes and compound **5** exhibits an interesting sweet, buttery flavor.

KEYWORDS: Green tea; *Camellia sinensis*; 3-methyl-2,4-nonanedione; 3-hydroxy-3-methyl-2,4-nonanedione; 1-methyl-2-oxopropyl hexanoate; 1-methyl-2-oxoheptyl acetate; 2-butyl-4,5-dimethyl-3(2*H*)-furanone; new constituents

INTRODUCTION

Guth and Grosch mentioned 3-methyl-2,4-nonanedione (**1**) (Figure 1) for the first time as off-flavor in reversed soybean oil (1). The same authors identified it as a compound with beneficial odor contribution in tea (2). In addition to its previous identification in dry spinach (3), we found it in fresh spinach leaves and described its organoleptic properties (4). Very recently, Kumasawa et al. (5) protected its use in green tea with a patent, and recently, it got the FEMA-number 4057 which opened its use in flavor creations. Amado et al. (6–8) published a series of investigations about its light-induced oxidation and autoxidation in model reactions as well as in green tea and established its relationship with furan fatty acids. The structure of 3-hydroxy-3-methyl-2,4-nonanedione (**2**) (Figure 1) was proposed on the basis of its mass and infrared spectra (8).

In the present study, extracts of brews of Chinese Long Jing, a famous green tea from Zhejiang province, and of Japanese Kiyosawa tea, a rare Japanese “Sen-cha” from a small tea garden, were prepared by solid-phase extraction and analyzed in search of compounds which would contribute to the characteristic green, woody, and haylike flavor of green tea. The structures of the new compounds were established by interpretation of the mass spectra and were confirmed by syntheses. Their organoleptic properties were evaluated.

EXPERIMENTAL PROCEDURES

Materials. Long Jing tea was received from Zhejiang province (China), and Kiyosawa (Sen-cha) was purchased from Betjeman & Barton (Carouge/Switzerland). OASIS-HLB cartridges were obtained from Waters Corporation (Milford, MA, 20 mL), filled with 1 g of the polymer [poly(divinylbenzene-co-*N*-vinylpyrrolidone)]. Silica gel (35–70 μ m, SDS, France) was deactivated with 50% water.

Preparation of Tea Extracts. Tea leaves (50 g) were brewed in demineralized water (500 mL) at 70 °C for 8 min. The leaves were filtered off through a cotton plug. The tea infusion (350 mL) was immediately cooled down to room temperature. An OASIS-HLB-cartridge (20 mL/1 g) was conditioned as follows: under a slight vacuum, methanol (10 mL) and then water (10 mL) were passed through. The cooled tea was loaded under vacuum (water pump), and then the cartridge was rinsed with water (100 mL) and with water containing 5% methanol (10 mL). The tea extract was eluted with ether (25 mL), which was dried and concentrated.

GC–MS Analysis. GC–MS was performed on a GC 6890 (Agilent, Palo Alto, CA) equipped with a 30 m \times 0.25 mm i.d. fused silica Supelcowax polar capillary column, film thickness 0.25 μ m, held at 50 °C for 5 min, then increased at 5 °C/min. to 240 °C, coupled to a MS 5972 (Agilent) or on a GC 6890 equipped with a 30 m \times 0.25 mm i.d. SPB-1 apolar column, film thickness 1 μ m, held at 60 °C for 5 min, then increased at 5 °C/min. to 250 °C, coupled to a MS 5971 (Agilent). The carrier gas was He (63 kPa) for both systems. The mass spectra in the electron impact mode (EI) were measured at 70 eV in a scan range from 35 to 300.

NMR Spectra. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker DPX 400 instrument with tetramethylsilane as internal standard, δ = 0.00 ppm (coupling constants *J* in Hz). Pulse sequence: power-gated decoupled ¹³C experiments with 30° excitation pulse (decoupling scheme WALTZ16); multiplicity was obtained from

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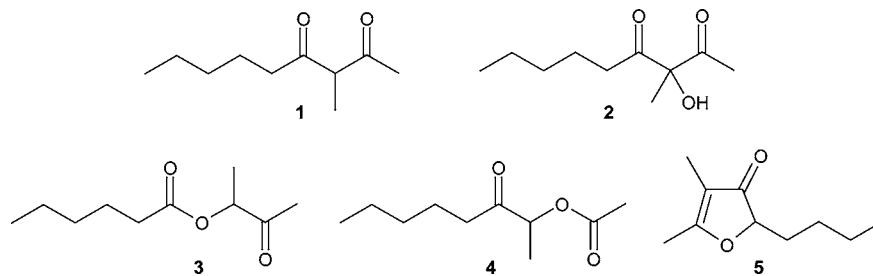


Figure 1. Compounds related to 3-methyl-2,4-nonanedione (**1**).

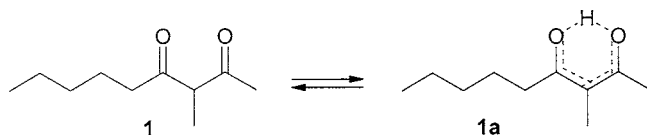


Figure 2. Diketone **1** and its enol.

DEPT90 and DEPT135 experiments, with 1 s recycle delay, 26000 Hz sweep width, 32768 data-points, and 1.5 Hz line-broadening. CoSY, ^{13}C , ^1H HSQC, and ^{13}C , ^1H HMBC-experiments were performed on a Bruker ADVANCE 500 MHz at 25 °C under standard conditions with coherence selection by gradients and a number of increments of 256.

Linear Retention Indices (RI). RI were determined after injection of a series of *n*-alkanes under the same conditions.

Syntheses. *3-Methyl-2,4-nonanedione (1)*. See Figure 2. Using the method of Adams and Hauser (9), 2-butanone was acylated with hexanoic anhydride using stoichiometric amounts of $\text{BF}_3 \cdot \text{AcOH}$. A mixture of β -diketone **1** and the corresponding enol **1a** in a ratio 3:1 was obtained (yield 53%). Analytical data follow for **1**. MS: m/z 170 (M^+ , 3), 155 (1), 152 (1), 127 (1), 114 (4), 99 (78), 86 (5), 71 (40), 55 (12), 43 (100); ^1H NMR: was consistent with previous reports (1); ^{13}C NMR: 207.4 (s); 205.2 (s); 61.7 (d); 41.7 (t); 31.3 (t); 28.5 (q); 23.2 (t); 22.4 (t); 13.9 (q); 12.7 (q); RI_{polar} : 1725; $\text{RI}_{\text{apolar}}$: 1211. Analytical data follow for **1a**. MS: m/z 170 (M^+ , 10), 155 (7), 152 (5), 137 (2), 127 (6), 114 (14), 99 (100), 85 (4), 71 (15), 55 (10), 43 (66). ^1H NMR: consistent with literature data (1). ^{13}C NMR: 193.5 (s); 190.3 (s); 104.4 (s); 35.9 (t); 31.6 (t); 25.0 (t); 23.5 (q); 22.5 (t); 14.0 (q); 12.6 (q). $\text{RI}_{\text{apolar}}$: 1295. The compound was unstable on a polar column.

3-Hydroxy-3-methyl-2,4-nonanedione (2). See Figure 3. This compound was prepared using the general method of Ramirez et al. (10) for analogous structures.

2,2,2-Trimethoxy-4,5-dimethyl-1,3,2-dioxaphosphole (6). In a dried flask, 2,3-butanedione (17.20 g, 0.20 mol, Fluka) was added very slowly (exothermic!) at 0–5 °C to trimethyl phosphite (27.28 g, 0.22 mol). The reaction mixture was stirred at room temperature overnight and then distilled (40–47 °C/0.1 Torr) using a Vigreux column to give pure **6** (35.04 g, yield: 83%).

Spectroscopic data of **6** were consistent with literature data (10)

(\pm)-*1-Acetyl-1-methyl-2-oxoheptyl dimethyl phosphate (7)*. In a dried flask, hexanoyl chloride (21.52 g, 0.16 mol, Fluka) was added dropwise at room temperature to **6** (33.6 g, 0.16 mol). The reaction mixture was stirred at 80 °C overnight (19 h) and became dark brown. Volatile byproducts were distilled off from 65 to 83 °C at 0.26 Torr, using a Vigreux column, and the residue which contained the desired product was bulb-to-bulb distilled (180 °C/0.15 Torr). Compound **7** (14.22 g) in a purity of ca. 80% by GC–MS was recovered (yield: 30%). A byproduct which was isolated by chromatography on deactivated silica gel using pentane with 10% ether as solvent was characterized as (\pm)-2-butyl-4,5-dimethyl-3(2H)-furanone (**5**, purity: >95%). Analytical data follow for **7**. MS: m/z 294 (M^+ , 0), 252 (3), 196 (28), 127 (100), 109 (12), 79 (2), 43 (15); ^1H NMR: 0.89 (t, $J = 6$, 3H); 1.20–1.35 (m, 4H); 1.56 (m, 2H); 1.84 (s, 3H); 2.27 (s, 3H); 2.62 (m, 2H); 3.85 (dd, $J = 10$, 6H); ^{13}C NMR: 204.5 (s); 202.2 (s); 93.1 (s); 54.7 (q); 54.6 (q); 37.5 (t); 31.1 (t); 25.6 (q); 22.8(t); 22.4 (t); 20.3 (q); 13.9(q); ^{31}P NMR: -1.9 (s), (ref 85% H_3PO_4). Analytical data follow for **5**. MS: m/z 168 (M^+ , 18), 125 (60), 112 (100), 97 (4), 83 (8), 54 (13), 43 (3); ^1H NMR: 0.91 (t, $J = 6$, 3H); 1.38 (m, 4H); 1.62 (m, 1H); 1.66 (s, 3H); 1.91 (m, 1H); 2.19 (s, 3H); 4.33(dd, $J = 7.5$ and 3.7, 1H); ^{13}C NMR: 205.2 (s); 184.7 (s); 110.8 (s); 84.7 (d); 31.0 (t); 26.9 (t); 22.4 (t); 14.9 (q); 13.9 (q); 5.6 (q). RI_{polar} : 1792; $\text{RI}_{\text{apolar}}$: 1277; UV: 272 nm ($\epsilon = 6181$) in EtOH; IR (neat): 1698, 1613 cm^{-1} .

(\pm)-*3-Hydroxy-3-methyl-2,4-nonanedione (2)*. In a flask, **7** (7.35 g at 80% purity, 20 mmol), H_2O (6.25 mL) and toluene (30 mL) were refluxed for 2 h. After the reaction mixture was cooled to room temperature, the water phase was separated, saturated with NaCl and extracted with toluene (3x). The combined organic extracts were dried over MgSO_4 . The solvent was removed using a Rotavapor and the residue (6.33 g) purified on deactivated silica gel using pentane/10% ether as solvent to give pure **2** (1.97 g, yield: 53%). Analytical data follow for **2**. MS was consistent with literature (8); ^1H NMR: 0.88 (t, $J = 6.5$, 3H); 1.26 (m, 4H); 1.54 (m, 2H); 1.53 (s, 3H); 2.23 (s, 3H); 2.49 (m, 1H); 2.66 (m, 1H); 4.73 (s, 1H); ^{13}C NMR: 209.6 (s); 207.4 (s); 87.6 (s); 36.8 (t); 31.2 (t); 24.6 (q); 23.1 (t); 22.7 (q); 22.4 (t); 13.9 (q). RI_{polar} : 1712; $\text{RI}_{\text{apolar}}$: 1201.

(\pm)-*1-Methyl-2-oxopropyl hexanoate (3)*. This compound was synthesized by analogy to the method of Long (11) (Figure 4).

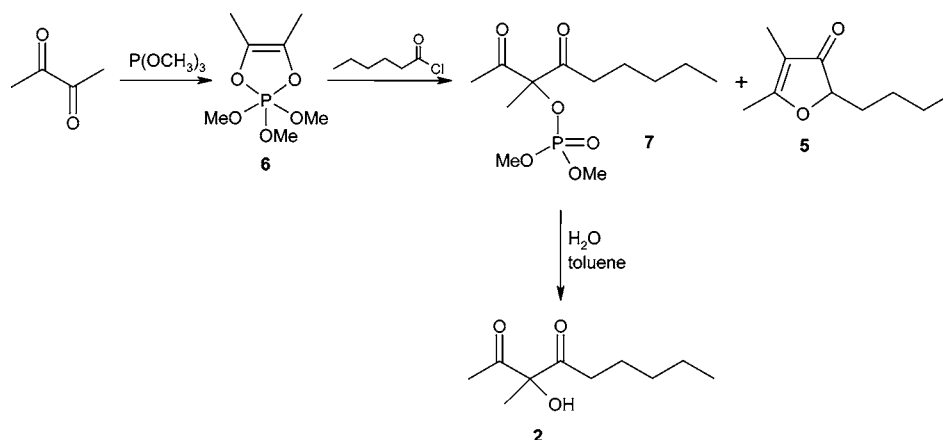


Figure 3. Synthesis of compounds **2** and **5**.

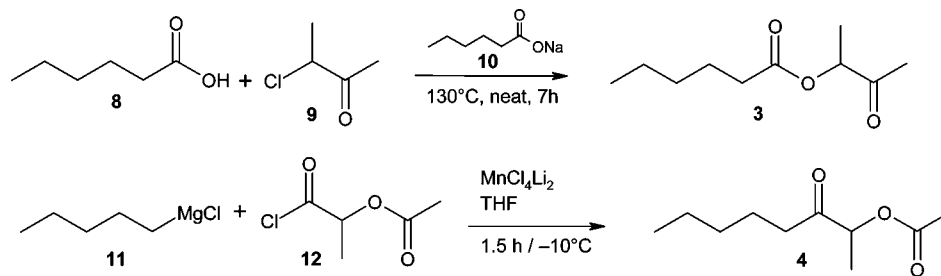


Figure 4. Syntheses of compounds 3 and 4.

Sodium Hexanoate (10). NaOH (20 g, 0.5 mol) in H₂O (80 mL) was introduced into a flask cooled in an ice/water bath. Hexanoic acid (**8**, 58.0 g, 0.5 mol) was added dropwise. After warming to room temperature the mixture (pH 8) was washed with ether to remove any free acid. The sticky salt was dried and reduced to a fine powder with a mortar.

Ester 3. Sodium salt **10** (13.8 g, 0.1 mol), hexanoic acid (**8**, 23.2 g, 0.2 mol), and 3-chloro-2-butanone (**9**, 10.65 g, 0.1 mol) were heated at 130 °C for 7 h. The reaction mixture was cooled to room temperature. Ether was added, and the mixture was cooled with an ice bath. Saturated aqueous Na₂CO₃ was added, and the mixture was stirred for 15 min. The two phases were separated, and the aqueous phase was extracted with ether. The combined organic phases were washed with water, dried with MgSO₄, and concentrated. The residue (7.16 g) was distilled at 67–72 °C at 12 mmHg using a Vigreux column to give compound **3** (9.59 g, 90% purity). Analytical data follow for **3**. MS: *m/z* 186 (M⁺, 1), 168 (0.5), 143 (8), 130 (2), 99 (85), 88 (4), 71 (38), 55 (10), 43 (100); ¹H NMR: 0.91 (t, *J* = 6.5, 3H); 1.33 (m, 4H); 1.40 (d, *J* = 6.5, 3H); 1.66 (m, 2H); 2.17 (s, 3H); 2.39 (m, 2H); 5.08 (q, 1H); ¹³C NMR: 205.8 (s); 173.2 (s); 74.7 (d); 34.0 (t); 31.3 (t); 25.7 (q); 24.5 (t); 22.3 (t); 16.0 (q); 13.9 (q); RI_{polar}: 1714; RI_{apolar}: 1233.

(±)-1-Methyl-2-oxoheptyl Acetate (4). See Figure 4. This compound was prepared by partially following a general method of Cahiez and Metais (12). In a flask dried with the flame under argon, a solution of MnCl₄Li₂ was prepared by stirring anhydrous MnCl₂ (6.93 g, 55 mmol) and anhydrous LiCl (4.68 g, 110 mmol) in THF (80 mL) at room

temperature for 2 h. Then, pentylmagnesium chloride (**11**), prepared under standard conditions (53 mmol) in THF (20 mL), was added dropwise at –10 °C. After 15 min, the reaction mixture was cooled to –20 °C, and 2-acetoxypropanoyl chloride (**12**), prepared according to Plieninger et al. (13) with thionyl chloride at 90 °C, was added dropwise. The reaction was stopped after 1.5 h, and the mixture was hydrolyzed with 1 N HCl at –10 °C, extracted with ether, washed with brine, dried over MgSO₄, and concentrated. The crude residue (8.76 g) was decolorized with active charcoal and distilled at 108–111 °C/12 mmHg to give 3.74 g of compound **4** (purity 95%). Analytical data follow for **4**. MS: *m/z* 186 (M⁺, 1), 144 (2), 130 (3), 126 (2), 99 (40), 87 (8), 71 (20), 55 (4), 43 (100); ¹H NMR: 0.89 (t, *J* = 6, 3H); 1.30 (m, 4H); 1.39 (d, *J* = 6.5, 3H); 1.60 (quint, 2H); 2.14 (s, 3H); 2.47 (m, 2H); 5.09 (q, *J* = 6.5, 1H); ¹³C NMR: 207.9 (s); 170.5 (s); 74.7 (d); 38.2 (t); 31.3 (t); 22.9 (t); 22.4 (t); 20.8 (q); 16.2 (q); 13.9 (q). RI_{polar}: 1703; RI_{apolar}: 1227.

RESULTS AND DISCUSSION

It is well-known that the flavor of tea extracts prepared by simultaneous distillation extraction (SDE) is always too rich in floral notes due to high amounts of terpenic alcohols such as linalool, geraniol, nerolidol, and phenylethanol formed by the hydrolysis of their glycosides under SDE conditions (14, 15). Therefore, our extracts of fresh tea brews were prepared by

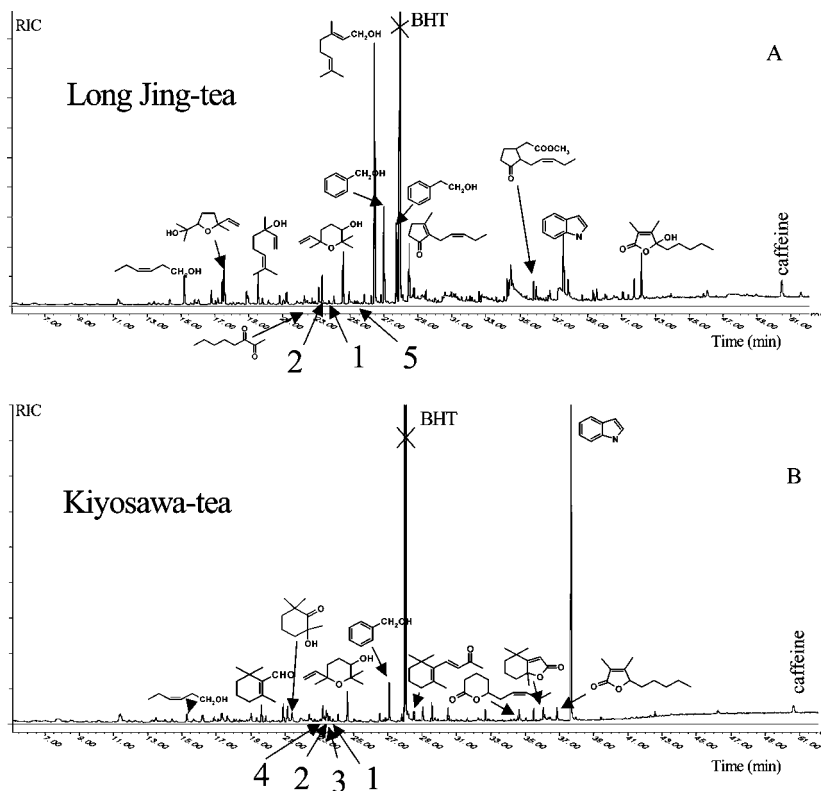


Figure 5. (A) GC–MS profile of an extract of Long Jing green tea. (B) GC–MS profile of an extract of Kiyosawa green tea. Both samples were analyzed on the Supelcowax column. BHT is an impurity of ether used for the extraction of the resin.

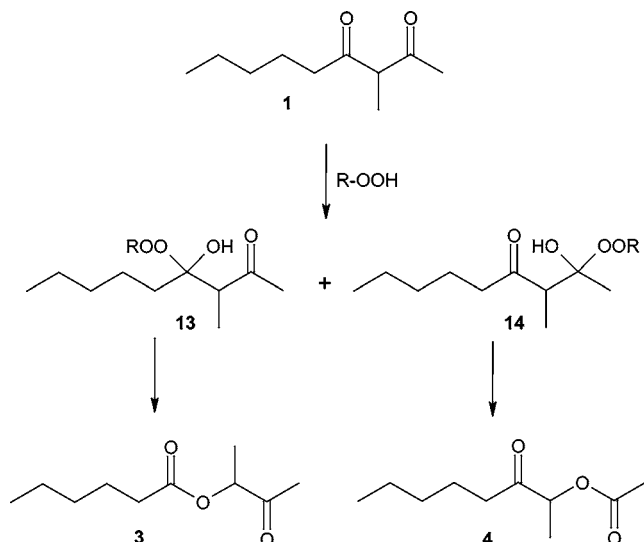


Figure 6. Formation of compounds 3 and 4.

solid-phase extraction and truly represented their original organoleptic properties.

In green tea processing, the fresh tea leaves undergo a slight fermentation which induces the degradation of nonvolatile constituents such as carotenes, amino acids, and fatty acids into flavor-active volatile compounds. Then, the enzymatic activity is stopped either by steaming or pan-firing before the leaves are dried. General knowledge about the complex chemistry of the tea flavor is summarized by Yamanishi (16). In the present paper, only the newly identified compounds will be described in detail.

The extract of Long Jing tea (Figure 5A), a pan-fired tea, had a delicate, green, slightly toasted, slightly spinachlike, floral, and sweet flavor and contained the so-called primary compounds (*Z*)-3-hexen-1-ol, linalool and its oxides, benzyl alcohol, phenylethanol, and geraniol, and especially jasmone and methyl jasmonate.

The extract prepared from Kiyosawa tea (Figure 5B), a steamed tea, exhibited a fresh, floral, green, slightly vegetable-like, and haylike aroma. Its main component was indole. Further components were the carotenoids β -cyclocitral, 2-hydroxy-2,6,6-trimethylcyclohexanone, β -ionone, and dihydroactinidiolide together with (*Z*)-3-hexen-1-ol, benzyl alcohol, linalool, and linalool oxide, the primary products, which are already present in extracts of fresh, unprocessed tea leaves (17).

Intrigued by the results of Amado and co-workers (7, 8) who investigated the photo-oxidative degradation of furan fatty acids in green tea and other dried vegetables, we concentrated our research on products they found so far, and indeed, compounds 1 and 2 were present in both extracts. In order to corroborate the structure of compound 2, a synthetic sample was prepared following a method of Ramirez et al. (10) (Figure 3). Addition of 2 to tea flavors improved their sweet, creamy, buttery notes and enhanced the typical mouthfeel of green tea.

The Kiyosawa extract contained the two compounds 3 and 4. Their structures could be established by their mass spectra and were confirmed by syntheses using known methodologies (Figure 4) (11, 12). The flavors of both compounds are reminiscent of green tea with floral, juicy, citruslike, and woody undertones. To the best of our knowledge, esters 3 and 4 are new structure types in tea chemistry, and mechanistic considerations suggest their origin from compound 1 (Figure 6). Addition of a peroxide to 1 to give the hydroperoxides 13 and 14 followed by a Baeyer–Villiger type rearrangement would

lead to the esters 3 and 4. The same type of rearrangements was observed by House et al. (18) when they treated β -diketones with peracids. Another example of a Baeyer–Villiger oxidation occurring in natural products is menthone lactone, which is formed from menthone and has been identified in *Mentha piperita* (19). Ester 3 is already known as a constituent of the pawpaw fruit (20), where it can be considered as an ester between hexanoic acid and acetone, both common compounds of fruit flavors. To our knowledge, ester 4 is a new natural product.

Furanone 5 was identified in our Long Jing tea extract as well as in a sample of white tea (Yin Zen) in very tiny amounts (unpublished results). It was also obtained as a byproduct of the reaction depicted in Figure 3. Its structure could be unambiguously determined by its ^{13}C NMR value at 205.2 ppm together with CoSY, ^{13}C , ^1H HMBC, and ^{13}C , ^1H HSQC experiments, the UV absorption at 272 nm ($\epsilon = 6181$) characteristic for conjugated ketones, the IR-band (at 1700 cm^{-1} for α,β -unsaturated cyclopentanones), and the mass spectrum (M^+ 168, $M^+ - 56$). Compound 5 exhibits a strong buttery, sweet, and creamy flavor.

2,3-Octanedione and hydroxy-bovalide, both reported to form in the photo-oxidation of furan fatty acids as well (7, 8), were additionally identified in our Long Jing extract.

In spite of the abundance of investigations published on the constituents of tea, the flavor of freshly brewed green tea still conceals many secrets. Nevertheless, combining the use of untraditional methods for the preparation of extracts with sophisticated GC-MS-analysis supported by synthetic work allowed the identification of three new compounds in tea, among them the two new structures 4 and 5, with interesting chemical structures and new organoleptic properties which help to increase the quality of ready-to-drink tea beverages, an increasingly important market in the flavor industry.

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