JARQ 48 (3), 355 - 362 (2014) http://www.jircas.affrc.go.jp

Subcritical Water Extraction of Low-molecular-weight Phenolic Compounds from Oil Palm Biomass

Fumio KAWAMURA[1, 6]*, Nur Syahirah SAARY[2], Rokiah HASHIM[2], Othman SULAIMAN[2], Koh HASHIDA[3], Yuichiro OTSUKA[3], Masaya NAKAMURA[4] and Seiji OHARA[5]

[1] Department of Forestry, Japan International Research Center for Agricultural Sciences (JIRCAS) (Tsukuba, Ibaraki 305-8686, Japan)
[2] Division of Bio-resource, Paper and Coatings Technology, School of Industrial Technology, Universiti Sains Malaysia (USM) (11800 Minden, Penang, Malaysia)
[3] Department of Biomass Chemistry, Forestry and Forest Products Research Institute (FFPRI) (Tsukuba, Ibaraki 305-8687, Japan)
[4] Department of Applied Microbiology, FFPRI (Tsukuba, Ibaraki 305-8687, Japan)
[5] FFPRI Fellow (Tsukuba, Ibaraki 305-8687, Japan)

Abstract

Subcritical water extraction of low-molecular-weight phenolic compounds from oil palm biomass (trunk, bark, petiole, rachis, leaves, empty fruit bunch fiber, midrib spine leaflets, stalk of fruit bunches, flesh, kernel shells, and albumen) was conducted. It was elucidated that gallic acid, protocatechuicaldehyde, *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, vanillic acid, syringic acid, vanillin, syringaldehyde *p*-coumaric acid and ferulic acid, all of which could be used as 2-pyrone-4,6-dicarboxylic acid (PDC) precursors, were contained in all parts of oil palm, although their composition differed. The peak yield of *p*-hydroxybenzoic acid was obtained among the PDC precursors. With regard to extraction conditions, temperature: 200°C, time: 20-60 min, and liquor ratio: 50-125 were the most efficient. The kernel shell exhibited the highest yield of PDC precursors, followed by the trunk, empty fruit bunch fiber, and bark. The results of our study indicate the oil palm is a potentially valuable source of PDC precursors.

Discipline: Forestry and forest products
Additional key words: *Elaeis guineensis*, Malaysian biomass, *p*-hydroxybenzoic acid, 2-pyrone-4, 6-dicarboxylic acid precursors

Introduction

The oil palm, *Elaeis guineensis* Jacq. (Arecaceae) is commercially significant owing to the production of palm oil and palm kernel oil derived from its fruit's flesh (mesocarp) and kernel, respectively (Corley & Tinker 2007). Although the oil palm is native to West Africa, it is mainly cultivated in Malaysia, Indonesia, East Africa, and South America (Blaizat & Cuvier 1953). Malaysia is one of the world's leading producers of palm oil with a current planted area of approximately 4.0 million ha. The oil palm was planted commercially for the first time in 1917 in Peninsular Malaysia, where it replaced rubberwood plantations and forests (Fitzherbert et al. 2008). A huge amount of residue is generated while cultivating the oil palm. The main residue in the field is the frond pruned while harvesting fresh fruit bunches. The trunk is the second most common residue after the frond, and a large amount is generated approximately 25 years after planting, because the trunk is clear-cut to prevent a decrease in fruit yield. The quantity of pruned frond is approximately 20 million t/year in oven-dried weight, followed by the trunk and empty fruit bunch (EFB) (each of which approximately 3 million t/year)(Basiron & Husin 1997, Husin 2000).

The fruit yield is approximately 180 kg/palm per year. As residue, the kernel shell accounts for 30% of the fruit biomass in oven-dried weight (Lee et al. 1990), and the

---

Present address:
[6] Department of Biomass Chemistry, FFPRI (Tsukuba, Ibaraki 305-8687, Japan)
*Corresponding author: e-mail chw@affrc.go.jp

Received 27 March 2012; accepted 28 October 2013.

quantity corresponds to double the extracted flesh fiber (Guo et al. 2008). The content of lignin in the kernel shell is high (Abnisa et al. 2011); hence numerous low-molecular-weight phenolic compounds are expected to be formed by lignin hydrolysis, although the quantity of kernel shell generated by mills is less than that of EFB.

The utilization of the oil palm biomass is restrictive, despite its abundance, as mentioned above. With regard to commercial utilization, the outer and middle parts of the trunk (without the bark) are used to manufacture plywood (Abdul Khalil et al. 2010, Sulaiman et al. 2008), although the inner part of the trunk (within a radius of around 30% from the center) is discarded because it lacks sufficient mechanical strength. Charcoal and wood vinegar are produced from the palm kernel shell (Cheah & Hoi 1999, Corley & Tinker 2007). The frond is used as fodder, albeit on a small scale (Kawamoto et al. 1999), while the extracted flesh fiber and kernel shell are mainly used as fuel for energy (Husain et al. 2002). Investigations into the manufacture of pulp and paper from EFB (Jiménez et al. 2009, Leh et al. 2008), and bio-ethanol production from sap obtained by squeezing old oil palm trunks felled for replanting (Kosugi et al. 2010) are ongoing; however, their commercialization remains insufficient to date.

Knowledge of phenolic constituents in each part of the oil palm is limited, and that in kernel shells is unclear. *p*-Hydroxybenzoic acid, *p*-hydroxybenzaldehyde, vanillic acid, syringic acid, vanillin, syringaldehyde, *p*-coumaric acid and ferulic acid were identified as alkaline degradation products of EFB (Sun et al. 2000). However, the behavior of these C_6-C_1 low-molecular-weight phenolic compounds during subcritical water extraction has not yet been elucidated. Phenolic constituents in the oil palm, which were identified by a chromatographic method without degradation, were as follows: three flavonoids (C_6-C_3-C_6 compounds), chrysoeriol, luteolin and naringenin from leaves (Nyananyo et al. 2010); five C_6-C_1 low-molecular-weight phenolic compounds, gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, vanillic acid, syringic acid, and three C_6-C_3 low-molecular-weight phenolic compounds, caffeic acid, *p*-coumaric acid, ferulic acid from fruit (Neo et al. 2010); caffeoylshikimic acid (ester of C_6-C_3 low-molecular-weight phenolic compound and shikimic acid) from palm oil mill effluent (POME)(Sambanthamurthi et al. 2011). It had been elucidated that *p*-hydroxybenzoic acid exists not only as a free form but also as an ester form in a lignin molecule of the oil palm (Tomimura 1992), although the existing form of the other low-molecular-weight phenolic compounds is unclear.

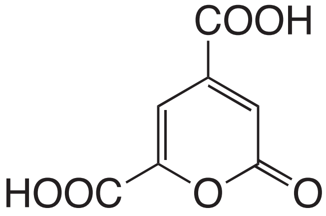

Fig. 1. Structure of 2-pyrone-4,6-dicarboxylic acid (PDC)

2-Pyrone-4,6-dicarboxylic acid (PDC) (Fig. 1) can be prepared using C_6-C_1 or C_6-C_3 low-molecular-weight phenolic compounds (e.g. *p*-hydroxybenzoic acid, protocatechualdehyde, syringaldehyde, vanillin, *p*-coumaric acid and ferulic acid; hereinafter referred to as “PDC precursors”) by fermentation using transgenic bacteria (Otsuka et al. 2006), and PDC can easily be converted into various useful polymers such as polyester, polyurethane, and polyamide. The conventional method used to prepare these PDC precursors is the alkaline nitrobenzene oxidation decomposition of lignin (Otsuka et al. 2006, Xiang & Lee 2001). The production of PDC using low-molecular-weight phenolic compounds extracted from oil palm biomass leads to the efficient utilization of unused bioresources as alternatives to non-renewable fossil resources.

It is important to hydrolyze ester linkages of the oil palm lignin to extract PDC precursors. Subcritical water treatment is considered advantageous because it does not use a reagent such as an alkali or acid, while subcritical water is maintained in a liquid state at temperatures between the boiling point of water under ambient conditions (100°C) and its supercritical point (374°C). The dielectric constant of subcritical water at 250°C resembles that of acetone at room temperature (Herrero et al. 2006, Wiboonsirikul et al. 2007). The dissociation constant of water varies with temperature; this property can be utilized to alter the extraction property of a number of substances. Accordingly, subcritical water has been employed to extract various substances, such as essential oils, proteins, xanthones, anthraquinones, flavonoids, and low-molecular-weight phenolic constituents (Buranov & Mazza 2009, Eikani et al. 2007, Ho et al. 2007, Kim et al. 2010, Kulkarni et al. 2008, Ozel et al. 2003, Petersson et al. 2010, Pongnaravane et al. 2006, Pourali et al. 2010, Prommuak et al. 2008, Sereewatthanawut et al. 2008, Srinivas et al. 2010). Subcritical water can function as an acid catalyst or base catalyst in chemical reactions because its dissociation constant exceeds that of ambient water; subcritical water dissociates into hydrogen and hydroxyl ions to a greater extent, thereby accelerating the reactions (Wiboonsirikul et al. 2007). Subcritical water is also employed to hydrolyze esters and polysaccharides without using additional catalysts (Asghari & Yoshida 2010, Fujii et al. 2006, Haghighat Khajavi et al. 2006, Khuwijitjaru et al. 2004). Subcritical water extraction has an advantage over supercritical water extraction in terms of equipment cost and energy consumption because the latter must be performed at a high

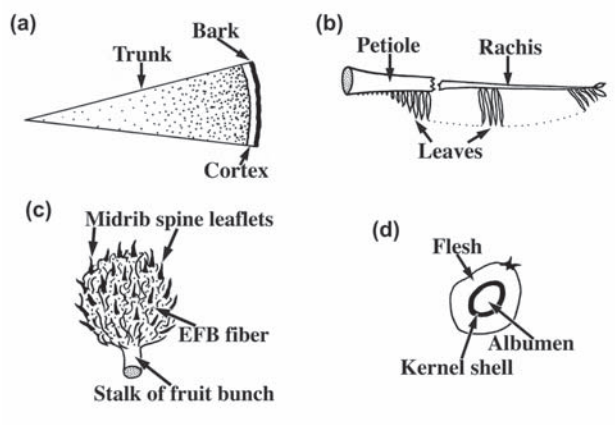

Fig. 2. Parts of the oil palm
a: cross-section of trunk, b: frond, c: empty fruit bunch, d: cross-section of fruit

Table 1. Moisture contents of sample meals

Parts	Moisture contents (%)
Trunk	8.7–9.8
Bark	11.0–11.2
Petiole	8.4–9.0
Rachis	9.0–9.8
Leaves	7.4
EFB fiber	8.5
Midrib spine leaflets	6.7
Stalk of fruit bunch	7.4
Flesh	2.5
Kernel shell	6.4
Albumen	6.1

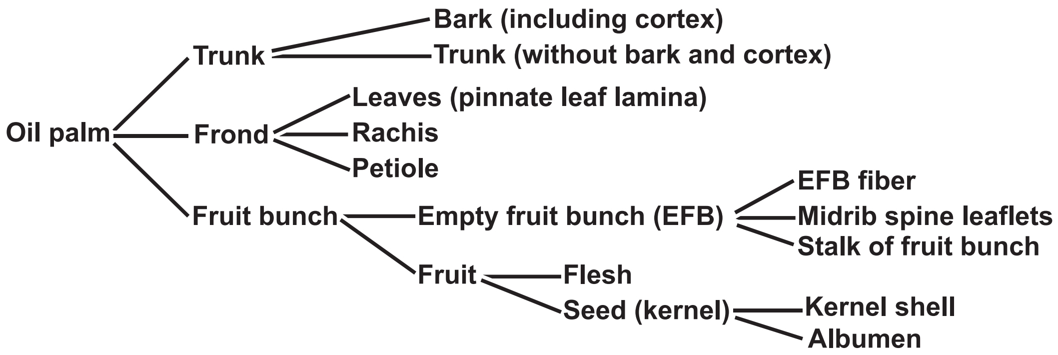

Fig. 3. Sample separation procedure

temperature (>374°C) and under high pressure (>22.4 MPa)(Zhang et al. 2007).

In this study, the optimum values of extraction temperature, extraction time and liquor ratio in the subcritical water extraction of each part of the oil palm biomass were determined, then the contents of PDC precursors obtained were also clarified. The potential of the oil palm as a raw material to prepare PDC precursors was assessed.

Materials and methods

1. Plant materials

A 33-year-old *Elaeis guineensis* (oil palm) cultivated in Staughton Estate, Redang Panjang, Perak, Malaysia, was sampled in May 2008. The cultivar was *dura* × *pisifera*. The oil palm sample was separated into 11 parts: trunk (without bark and cortex), bark, petiole, rachis, leaves, empty fruit bunch (EFB) fiber, midrib spine leaflets, stalk of fruit bunch, flesh, kernel shell, and albumen (Corley & Tinker 2007). Each part of the oil palm is illustrated in Fig. 2 and the sample separation procedure is shown in Fig. 3. The portion from the base to 50 cm of the frond stalk was treated as the petiole, and that from the top to 100 cm of the frond stalk as the rachis.

2. Sample meal preparation

All the raw plant materials were placed in a freezer at -20°C, cut into chips (*ca*. 25 × 6 × 3 mm) and freeze-dried. After freeze-drying, the chips were ground into meal in a Wiley mill (Retsch cutting mill SM 1). The sample meal was sieved and 250-500-µm particles were collected. The completely processed sample meal was then placed in a freezer at -20°C. Voucher specimens were deposited in the Division of Bio-resource, Paper and Coatings Technology, Universiti Sains Malaysia (USM).

3. Subcritical water extraction of PDC precursors from oil palm biomass

The equipment for subcritical water extraction comprises a temperature controller, band heater, pressure gauge, and pressure-tight cell TVS-1 (Taiatsu Techno Inc., Tokyo, Japan; capacity, 150 mL; maximum temperature, 200°C). Before subcritical water extraction was performed, the moisture content of each sample meal was determined (Table 1). Air-dried sample meal (1 g) was placed in the pressure-tight cell and distilled water (25-125 mL) was added. Subsequently, the pressure-tight cell was heated to 100-200°C over a period of 5-80 min (holding time). To raise the temperature of the cell (containing 100 mL water) from ambient temperature to extraction temperature, the cell was heated for 5, 8, 12, 16, 23, and 34 min to attain temperatures of 100, 120, 140, 160, 180, and 200°C, respectively. After extraction, the pressure-tight cell was cooled by water flow, whereupon the reaction products were centrifuged for 20 min at 6,000 rpm and the supernatant was filtrated using a DISMIC-13CP cellulose acetate filter (Toyo Roshi Inc., Tokyo, Japan; pore size, 0.45 μm). The filtrated solution (20 μL) was subjected to reversed-phase high-performance liquid chromatography (HPLC) analysis. Subcritical water extraction was repeated three times under each condition of temperature, time and liquor ratio, and the mean value and standard deviation were calculated.

4. HPLC method

HPLC was performed with a Shimadzu LC-20AD pump, a SPD-20A ultraviolet-visible (UV/VIS) detector, and CTO-20AC column oven, using a prepacked Shimadzu Shim-pack CLC-ODS (M) (250 × 4.6 mm i.d.) column. A linear gradient elution of Eluent A (10 mM aqueous phosphoric acid solution) and B (methanol) was used to perform the separation. The elution program was as follows [Eluent B% (min)]: 15% (0) - 20% (3) - 20% (20) - 50% (40). Solvents for HPLC were HPLC grade (Sigma-Aldrich Inc., St. Louis, MO, USA). The conditions for HPLC analyses were as follows: temperature of the UV/VIS cell, 40°C; temperature of the column oven, 40°C; wavelengths of the UV/VIS detector, 280 and 360 nm; and flow rate, 1.0 mL min^{-1}. The retention times (min) of 14 PDC precursors are summarized in Table 2. Quantitative determination using HPLC was carried out with the calibration curves previously prepared using the absorbance of standard materials at 280nm. The yields of PDC precursors from the plant materials were calculated as percentage values based on oven-dried sample meal. The qualitative determination of each PDC precursor from the plant materials was performed based on the retention time and the precursor's UV spectrum recorded using an UV scan of each peak. Each sample solution was subjected to HPLC analyses within 4 h of subcritical water extraction to prevent any decline in quality.

Results and discussion

1. Optimum conditions for subcritical water extraction of PDC precursors from the oil palm trunk and their transformation behavior

Ten PDC precursors, gallic acid, protocatechuicaldehyde, *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, vanillic acid, syringic acid, vanillin, syringaldehyde, *p*-coumaric acid and ferulic acid were detected in subcritical water extraction products from the oil palm trunk. The effect of temperature on the PDC precursor yields in subcritical water extraction is shown in Fig. 4a (total PDC precursor, *p*-hydroxybenzoic acid), Fig. 4b (syringaldehyde, protocatechuicaldehyde, syringic acid, vanillin) and Fig. 4c (gallic acid, *p*-hydroxybenzaldehyde, vanillic acid, *p*-coumaric acid, ferulic acid). The maximum total yield of the PDC precursors was attained at 200°C, and *p*-hydroxybenzoic acid was obtained in the highest yield among the ten precursors, while gallic acid and *p*-coumaric acid disappeared at this temperature (eight PDC precursors were detected at 200°C).

Table 2. Retention times of PDC precursors in HPLC

PDC precursors	Retention times (min)[a]
Gallic acid	5.18
3,4,5-Trihydroxy-benzaldehyde	6.93
Protocatechuic acid	8.79
Protocatechualdehyde	11.25
p-Hydroxybenzoic acid	13.59
p-Hydroxybenzaldehyde	16.84
Vanillic acid	17.76
Caffeic acid	18.33
Syringic acid	21.88
Vanillin	22.57
Syringaldehyde	27.87
p-Coumaric acid	30.56
Ferulic acid	34.49
Sinapic acid	35.75

[a] Determined using reference standards.

The yield of gallic acid was highest at 100°C, declined at temperatures above 100°C and disappeared at 180°C (Fig. 4c). Most of the other precursors exhibited maximum yield at 200°C; however, *p*-coumaric acid, syringaldehyde, and ferulic acid exhibited maximum yield at 160°C (Figs. 4b and 4c). There was a significant rise in the yield of *p*-hydroxybenzoic acid with increasing treatment temperature, particularly at 200°C (Fig. 4a). It was assumed that *p*-hydroxybenzoic acid is relatively stable when heated, as compared to gallic acid, which has a pyrogallol nucleus in a molecule, and that *p*-hydroxybenzoic acid is formed during subcritical water extraction by hydrolyzing *p*-hydroxybenzoic acid esters existing in lignin molecules(Haghighat Khajavi et al. 2006, Khuwijitjaru et al. 2004, Pourali et al. 2010, Tomimura 1992). Tannins and other components are also potentially the origin of *p*-hydroxybenzoic acid, which is formed by the hydrolysis of esters in tannin and other molecules (Nomizu et al. 2008). Wiboonsirikul et al. investigated the subcritical water extraction of defatted rice bran and found that the yield of

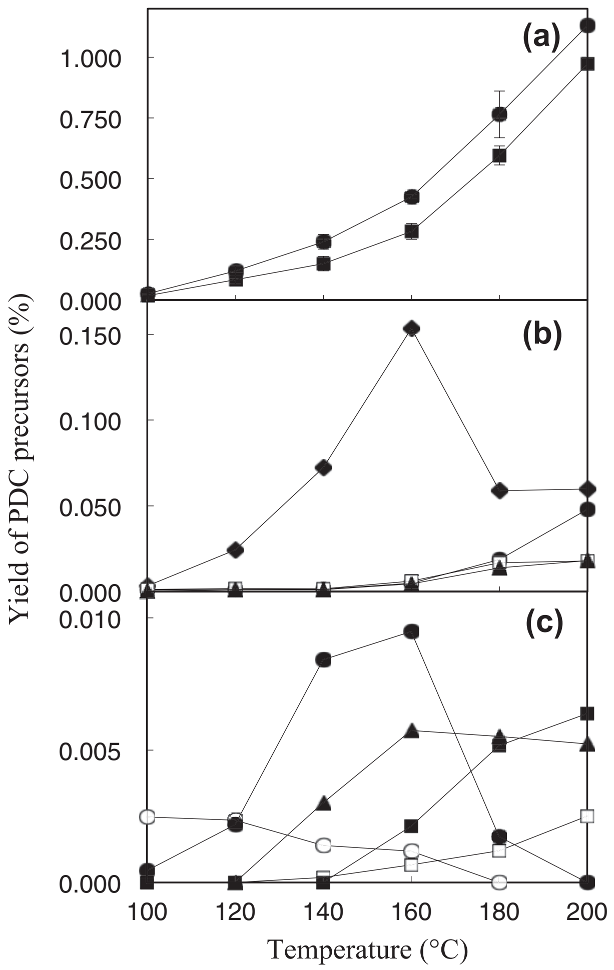

Fig. 4. Effect of temperature on the yields of PDC precursors from the oil palm trunk in subcritical water extraction

Conditions for extraction: time, 20 min; liquor ratio, 50. Results are expressed as the mean ± SD (n = 3, Fig. 4a).

(a) ●: Total PDC precursor, ■: *p*-hydroxybenzoic acid; (b) ◆: syringaldehyde, ●: protocatechuic-aldehyde, □: syringic acid, ▲: vanillin; (c) ○: gallic acid, □: *p*-hydroxybenzaldehyde, ■: vanillic acid, ●: *p*-coumaric acid, ▲: ferulic acid.

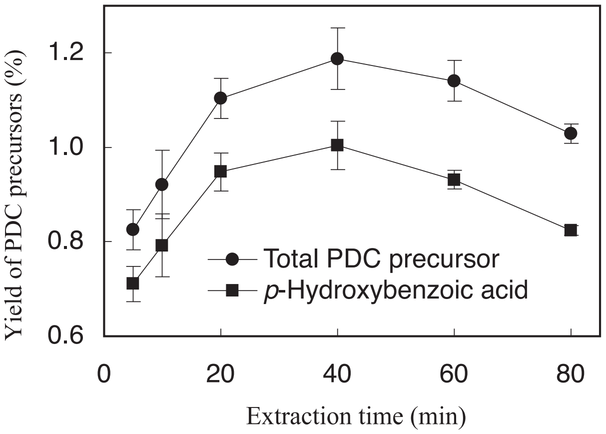

Fig. 5. Effect of time on the yields of PDC precursors from the oil palm trunk in subcritical water extraction

Conditions for extraction: temperature, 200°C; liquor ratio, 50. Results are expressed as the mean ± SD (n = 3).

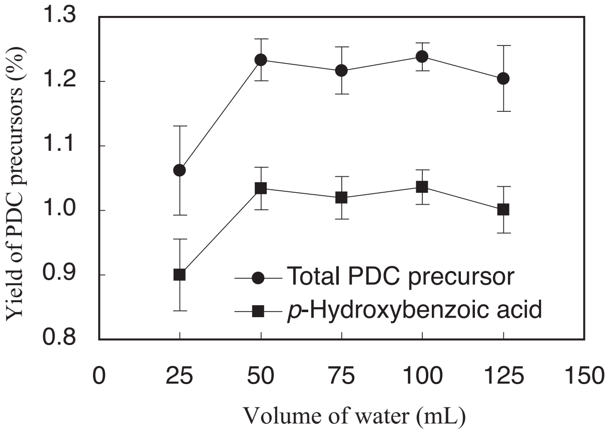

Fig. 6. Effect of water volume on the yields of PDC precursors from the oil palm trunk in subcritical water extraction

Conditions for extraction: temperature, 200°C; time, 40 min. Results are expressed as the mean ± SD (n = 3).

the extracts peaked at 200°C, and the total phenol content peaked at 200-250°C (Wiboonsirikul et al. 2007); these results resembled those we obtained for subcritical water extraction using the oil palm trunk.

The effect of extraction time on the yields of PDC precursors at 200°C is shown in Fig. 5. The highest total yield of PDC precursors and the highest yield of *p*-hydroxybenzoic acid were attained with an extraction time of 20-60 min. It was confirmed that the yield of PDC precursors was lower between 0 and 10 min due to the insufficient hydrolysis of *p*-hydroxybenzoic acid esters in lignin molecules. On the other hand, it was presumed that the decomposition of PDC precursors occurred within 80 min, because their yield decreased. We confirmed the effect of extraction time on the yields of each PDC precursor; *p*-hydroxybenzoic acid showed the highest yield among PDC precursors. Furthermore, *p*-hydroxybenzoic acid is estimated as a value-added compound, because it can be used not only as a PDC precursor but also as a raw material for manufacturing polyester plastics (Higashi et al. 1984a, Higashi et al. 1984b). Based on the significance of *p*-hydroxybenzoic acid, we described here only the yield of this compound and the total yield of PDC precursors.

The effect of water volume on the yields of PDC precursors at 200°C for 40 min is shown in Fig. 6. The yields of PDC precursors were high within the range 50-125 mL, while the yield was lower when using 25 mL water.

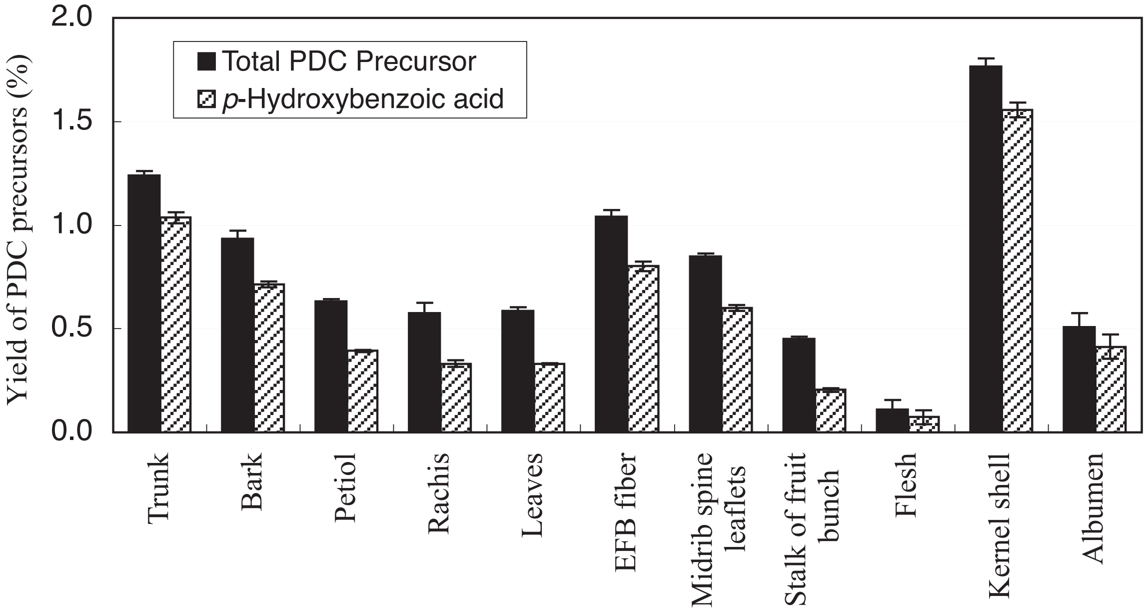

Fig. 7. Yields of PDC precursors from each part of the oil palm
Conditions for extraction: temperature, 200°C; time, 40 min; liquor ratio, 100. Results are expressed as the mean ± SD ($n = 3$).

From the results shown in Figs. 4-6, we concluded that the optimum conditions for subcritical water extraction of PDC precursors using oil palm trunk meal are extraction temperature of 200°C, extraction time of 20-60 min and liquor ratio of 50-125.

2. Yield of PDC precursors from each part of the oil palm

The yields of PDC precursors from each part of the oil palm are shown in Fig. 7; calculated based on the oven-dried weight of the oil palm meal. Subcritical water extraction was conducted at 200°C for 40 min using a liquor ratio of 100, and eight PDC precursors, protocatechuicaldehyde, *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, vanillic acid, syringic acid, vanillin, syringaldehyde, and ferulic acid were detected in the trunk, bark, petiole, rachis and leaves of the oil palm under this extraction condition. Seven PDC precursors other than ferulic acid were detected in the EFB fiber, midrib spine leaflets, fruit bunch stalk, flesh, kernel shell, and albumen.

The ratio of the yield of *p*-hydroxybenzoic acid to the total yield of PDC precursors was high in the waste derived from the fruit - flesh, kernel shell, and albumen, while low in the stalk of the fruit bunch and the three parts derived from the frond - petiole, rachis, and leaves. The yield of *p*-hydroxybenzoic acid and the total yield of PDC precursors were highest in the kernel shell, followed by the trunk, EFB fiber, and bark, while the yield of PDC precursors from the fruit flesh was the lowest.

The amount of oil palm kernel shells generated in Malaysia is the largest among the three forms of waste derived from fruits (Guo et al. 2008, Lee et al. 1990). Therefore the kernel shell, trunk, EFB fiber, and bark of the oil palm are anticipated to be potentially valuable sources of PDC precursors. The trunk and bark can be used without mutual separation because both exhibit high yields of PDC precursors.

The petiole, rachis and leaves of the frond contained the same amount of PDC precursors, while the average value of the content of PDC precursors was approximately 1/2 and 1/3 of the content in the trunk and kernel shell, respectively. However, the pruned frond resources constituted more than 6 times the amount of generated EFB and trunk (Basiron & Husin 1997). The total amount of PDC precursors in the petiole, rachis and leaves of the frond was calculated to exceed their amount in EFB or the trunk. Therefore, the frond was anticipated to be a valuable raw material for PDC precursors.

Conclusion

It was elucidated that a large amount of PDC precursors was contained in the oil palm. PDC precursors were readily extracted with subcritical water. Quantitative analyses of PDC precursors in each part of the oil palm revealed that their content is highest in the kernel shell. In consideration of the content of PDC precursors in each part of the oil palm and the abundance of each part, the petiole, rachis and leaves of the frond were evaluated to have great potential as a bioresource of PDC precursors.

Acknowledgments

This study was conducted as part of an international collaborative research project - “Woody biomass conversion into bio-composites and functional materials in the tropics” - between USM and the Japan International Research Center for Agricultural Sciences (JIRCAS); the study was funded by the Ministry of Agriculture, Forestry and Fisheries of Japan.

References

Abdul Khalil, H. P. S. et al. (2010) Development and material properties of new hybrid plywood from oil palm biomass. *Mater. Des.*, **31**, 417-424.

Abnisa, F. et al. (2011) Utilization possibilities of palm shell as a source of biomass energy in Malaysia by producing bio-oil in pyrolysis process. *Biomass & Bioenergy*, **35**, 1863-1872.

Asghari, F. S. & Yoshida, H. (2010) Conversion of Japanese red pine wood (*Pinus densiflora*) into valuable chemicals under subcritical water conditions. *Carbohydr. Res.*, **345**, 124-131.

Basiron, Y. & Husin, M. (1997) Availabillity, Extraction and Economics of Oil Palm Biomass Utilization. *In* Utilization of Oil Palm Tree, eds. Harun, J. et al., Oil Palm Tree Utilization Committee (OPTUC), Kuala Lumpur, Malaysia, 3-15.

Blaizat, P. & Cuvier, P. (1953) A new source of carotene: palm fiber oil from *Elaeis guineensis*. *J. Am. Oil Chem. Soc.*, **30**, 586-587.

Buranov, A. U. & Mazza, G. (2009) Extraction and purification of ferulic acid from flax shives, wheat and corn bran by alkaline hydrolysis and pressurised solvents. *Food Chem.*, **115**, 1542-1548.

Cheah, S. C. & Hoi, W. K. (1999) By-products for chemical, microbiological and other uses. *In* Oil palm and the environment – a Malaysian perspective, eds. Singh, G. et al., Malaysian Oil palm Growers’ Council, Kuala Lumpur, Malaysia, 241-252.

Corley, R. H. V. & Tinker, P. B. (2007) Chapter 1 and 2, the origin and development of the oil palm industry, the classification and morphology of the oil palm. *In* The oil palm, Fourth edition. Blackwell Science, Oxford, 1-52.

Eikani, M. H. et al. (2007) Subcritical water extraction of essential oils from coriander seeds (*Coriandrum sativum* L.). *J. Food Eng.*, **80**, 735-740.

Fitzherbert, E. B. et al. (2008) How will oil palm expansion affect biodiversity? *Trends Ecol. Evol.*, **23**, 538-545.

Fujii, T. et al. (2006) Decomposition kinetics of monoacyl glycerol and fatty acid in subcritical water under temperature-programmed heating conditions. *Food Chem.*, **94**, 341-347.

Guo, J. et al. (2008) Preparation of activated carbons by utilizing solid wastes from palm oil processing mills. *J. Porous Mater.*, **15**, 535-540.

Haghighat Khajavi, S. et al. (2006) Kinetics of maltooligosaccharide hydrolysis in subcritical water. *J. Agric. Food Chem.*, **54**, 3663-3667.

Herrero, M. et al. (2006) Sub- and supercritical fluid extraction of functional ingredients from different natural sources: Plants, food-by-products, algae and micoalgae. *Food Chem.*, **98**, 136-148.

Higashi, F. et al. (1984a) Direct polymeriztion of hydroxybenzoic acids by use of diphenyl chlorophosphate in the presense of N,N-dimethylformamide. *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2181-2187.

Higashi, F. et al. (1984b) Further study of the direct polycondensation reaction of hydroxybenzoic acids with tosyl chloride and N,N-dimethylformamide. *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 3607-3610.

Ho, C. H. L. et al. (2007) Extraction of lignans, proteins and carbohydrates from flaxseed meal with pressurized low polarity water. *LWT - Food Sci. Technol.*, **40**, 1637-1647.

Husain, Z. et al. (2002) Briquetting of palm fibre and shell from the processing of palm nuts to palm oil. *Biomass & Bioenergy*, **22**, 505-509.

Husin, M. (2000) Utilization of oil palm biomass for various wood-based and other products. *In* Advances in oil palm research, eds. Basiron, Y. et al., Malaysian Palm Oil Board, Ministry of Primary Industry, Kuala Lumpur, Malaysia, **2**, 1346-1412.

Jiménez, L. et al. (2009) Soda-anthraquinone pulping of palm oil empty fruit bunches and beating of the resulting pulp. *Bioresour. Technol.*, **100**, 1262-1267.

Kawamoto, H. et al. (1999) Effect of processing methods on digestibility and voluntary intake of oil palm frond in cattle. *Bull. Natl. Grassl. Res. Inst.*, **59**, 10-17.

Khuwijitjaru, P. et al. (2004) Kinetics on the hydrolysis of fatty acid esters in subcritical water. *Chem. Eng. J.*, **99**, 1-4.

Kim, W.-J.et al. (2010) Extraction of mangiferin from Mahkota Dewa (*Phaleria macrocarpa*) using subcritical water. *J. Ind. Eng. Chem.*, **16**, 425-430.

Kosugi, A. et al. (2010) Ethanol and lactic acid production using sap squeezed from old oil palm trunks felled for replanting. *J. Biosci. Bioeng.*, **110**, 322-325.

Kulkarni, A. et al. (2008) Antioxidant compounds from *Eucalyptus grandis* biomass by subcritical liquid water extraction. *J. Wood Sci.*, **54**, 153-157.

Lee, C. H. et al. (1990) Selection progress in the Deli *dura* population. *In* Proc. workshop ‘progress of oil palm breeding populations’, Palm oil Res. Inst. Malaysia, Kuala Lumpur, Malaysia, 81-89.

Leh, C. P. et al. (2008) Optimisation of oxygen delignification in production of totally chlorine-free cellulose pulps from oil palm empty fruit bunch fibre. *Ind. Crops Prod.*, **28**, 260-267.

Neo, Y.-P. et al. (2010) Phenolic acid analysis and antioxidant activity assessment of oil palm (*E. guineensis*) fruit extracts. *Food Chem.*, **122**, 353-359.

Nomizu, K. et al. (2008) Antioxidants from steamed used tea leaves and their reaction behavior. *Biosci. Biotechnol. Biochem.*, **72**, 1682-1689.

Nyananyo, B. L. et al. (2010) Phytochemical investigations of some tropical plants from the Niger delta area of Nigeria. *Sci. Africana*, **9**, 173-177.

Otsuka, Y. et al. (2006) Efficient production of 2-pyrone-4,6-dicarboxylic acid as a novel polymer-based material from protocatechuate by microbial function. *Appl. Microb. Biotechnol.*, **71**, 608-614.

Ozel, M. Z. et al. (2003) Subcritical water extraction of essential oils from *Thymbra spicata*. *Food Chem.*, **82**, 381-386.

Petersson, E. V. et al. (2010) Pressurized Hot Water Extraction of anthocyanins from red onion: A study on extraction and degradation rates. *Anal. Chim. Acta*, **663**, 27-32.

Pongnaravane, B. et al. (2006) Extraction of anthraquinones from roots of *Morinda citrifolia* by pressurized hot water:

Antioxidant activity of extracts. *In* The journal of supercritical fluids, 7th International Symposium on Supercritical Fluids, Orlando, Florida, **37**, 390-396.

Pourali, O. et al. (2010) Production of phenolic compounds from rice bran biomass under subcritical water conditions. *Chem. Eng. J.*, **160**, 259-266.

Prommuak, C. et al. (2008) Extraction of flavonoids and carotenoids from Thai silk waste and antioxidant activity of extracts. *Sep. Purif. Technol.*, **62**, 444-448.

Sambanthamurthi, R. et al. (2011) Oil palm vegetation liquor: a new source of phenolic bioactives. *Br. J. Nutr.*, **106**, 1655-1663.

Sereewatthanawut, I. et al. (2008) Extraction of protein and amino acids from deoiled rice bran by subcritical water hydrolysis. *Bioresour. Technol.*, **99**, 555-561.

Srinivas, K. et al. (2010) Solubility and solution thermodynamic properties of quercetin and quercetin dihydrate in subcritical water. *J. Food Eng.*, **100**, 208-218.

Sulaiman, O. et al. (2008) Evaluation on some finishing properties of oil palm plywood. *Holz Als Roh und Werkstoff*, **16**, 5-10.

Sun, R.-C. et al. (2000) Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre. *Polymer Degrad. Stabil.*, **68**, 111-119.

Tomimura, Y. (1992) Chemical characteristics and utilization of oil palm trunks. *JARQ*, **25**, 283-288.

Wiboonsirikul, J. et al. (2007) Properties of extracts from defatted rice bran by its subcritical water treatment. *J. Agric. Food. Chem.*, **55**, 8759-8765.

Xiang, Q. & Lee, Y. Y. (2001) Production of oxychemicals from precipitated hardwood lignin. *Appl. Biochem. Biotech.*, **91-93**, 71-80.

Zhang, S. et al. (2007) Economic assessment of fusion and fusion-driven subcritical systems based on internalization of external costs and benefits. *In* Fusion engineering and design, Proceedings of the 24th Symposium on Fusion Technology - SOFT-24, **82**, 2879-2884.