PALM-BASED CHIRAL COMPOUNDS

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ABSTRACT

Palm-based chiral compounds are of potential value although they are either taken for granted or largely ignored. This paper reports on the chirality features and optical activities of readily available palm-based chiral compounds such as asymmetrical acylglycerols, phospholipids, tocols, carotenoids and sterols.

Keywords: stereochemistry, chiral, optical rotation, crude palm oil.

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INTRODUCTION

In principle, all given atoms will interact with one another and can exist in an infinite variety of configurations. All of them will have different energies in the formation and breakdown of the relatively stable arrays that are termed *molecules*. These molecules constitute a given group of atoms, hence they have different configurations and energies. Energy minimal within this subset is defined as the isomers of the molecule.

Isomerism is one of the more subtle, fascinating and important aspects of chemistry as a whole and, when expressed in the phenomenon of chirality, it is one of the more singular features of life. The studies of stereochemistry involve the investigation of a three-dimensional valence-bond representation of the molecule on the basis of a ranking of ligands according to a sequence rule (Cahn, 1964). This has led to the stereochemical descriptions by an *R* or *S* symbol based on the Cahn-Ingold-Prelog (CIP) system (Cahn *et al*., 1966; 1970; Prelog and Helmchen, 1982).

A molecule that lacks all symmetry and is therefore termed asymmetric belongs to the class of chiral compounds. The chirality course involves the overall chirality of the possible chiral elements based on a particular feature. The contributing factors to the overall chirality could arise from four elements of symmetry, *i.e.* point, axis, interior planar and exterior mirror of symmetry (Cahn *et al*., 1966; Brown, 1975).

Stereochemistry plays an important role in the pharmaceutical industry. As most biologically active compounds have one or more stereocentres, their specific activities are usually related to only one isomer.

To date, chirality in palm oil components has not been fully explored (Renaud *et al*., 1995). The recent awareness of the possible applications of potential chiral compounds in palm oil has prompted us to look into this area, in line with the government-industry synergy of downstream value-added activities and strategies in the oil palm industry. The chiral compounds in the palm oil have, so far, not been exploited thus their potential uses or effects are of interest.

CHIRAL PALM OIL CONSTITUENTS

There are at least five groups of chiral compounds in palm oil, namely asymmetrical acylglycerols, phospholipids, tocols, carotenoids and sterols. These compounds can have several stereogenic centres.

Asymmetric Acylglycerols

Glycerols are prochiral molecules with the prochiral carbon atoms carrying two CH_2OH groups. When the glycerols are acylated with one, two or three fatty acid groups, acylglycerols are obtained, *i.e.* monoacylglycerols, diacylglycerols and triacylglycerols. They are the esters of glycerol and fatty acids in different combinations and compositions.

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The designation of the stereochemistry of acylated glycerol requires a stereospecific numbering system for the carbon atoms of glycerol molecules as defined in Fischer projection (Gunstone, 1996). The molecules that are numbered in this manner have the prefix *sn* preceding the term *glycerol*. Acylated glycerols will have the central carbons chiral when the fatty acid substituents at the *sn*-1, *sn*-3 or *sn*-1 and *sn*-3 positions are different. Hence, there is a wide spectrum of chiral mono-, di- and triacylglycerols. Chiral acylglycerol may exist as a pair of enantiomers. They are mirror-image molecules with equal but opposite optical activities. The equal mixture of both enantiomers is termed *racemic*.

Monoacylglycerols (monoglycerides, MG). Monoacylglycerols are fatty acid monoesters of glycerol. Their composition in crude palm oil is less than 1%. They exist in two isomeric forms as α- and β-isomers. A particular orientation of a single fatty acid moiety to any of the two carbon atoms, *sn*-1 or *sn*-3 of glycerol (α-isomer) causes the formation of two stereoisomers which could exist as a pair of enantiomers. The selected optical rotations of the chiral monoacylglycerols are tabulated in *Table 1* (Gunstone *et al*., 1994). No optical isomers could be obtained when the *sn*-2 carbon is acylated with a fatty acid (β-isomers) due to the molecular symmetry.

Diacylglycerols (diglycerides, DG). Diacylglycerols are fatty acid diesters of glycerol. They take up 2%-7% of the crude palm oil composition. The arrangement of two different fatty acid moieties to any two of the three carbon atoms (*sn*-1 and *sn*-2 or *sn*-1 and *sn*-3) results in two stereoisomers as α, β- and α, α'-isomers. Each stereoisomer exists as a pair of enantiomers. The substitution of two same fatty acids to carbon *sn*-1 and *sn*-2 forms chiral α, β-isomer but the substitution to carbon *sn*-1 and *sn*-3 gives achiral α, α'-isomer. The selected optical rotations of chiral diacylglycerols are given in *Table 2* (Gunstone *et al*., 1994).

Triacylglycerols (triglycerides, TG). Triacylglycerols are fatty acid triesters of glycerol. They form the major component in crude palm oil (more than 90%). The acylation of three or two different fatty acid moieties to the carbon atoms of glycerol results in the formation of several stereoisomers respectively.

The number of possible triacylglycerols in palm oil is dependent upon the number of acids present in the fatty acid pool (Gunstone, 1996). Hence, the triacylglycerol population exists in a variety of combinations. Considering only the major fatty acids in crude palm oil, *i.e.* palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2), it is documented that a total of 25

TABLE 1. OPTICAL ROTATIONS OF MONOACYLGLYCEROLS (MG)

Type of fatty acid substituents*	Specific rotation, $[\alpha]_D$ (solvent)	Configuration
P_ _	-4.3° (py)	*(R)*
S_ _	-34.1° (EtOH, 300 nm)	*(R)*
O_ _	-3.6° (py)	*(R)-(Z)*
L_ _	-5.2° (MeOH)	*(R)-(Z,Z)*
	+5.4° (MeOH)	*(S)-(Z,Z)*

Notes: *P-palmitic; S-stearic; O-oleic; L-linoleic.

TABLE 2. OPTICAL ROTATIONS OF DIACYLGLYCEROLS (DG)

Type of fatty acid substituents*	Specific rotation, $[\alpha]_D$ (solvent)	Configuration
PP_	-2.75° ($CHCl_3$)	*(S)*
PO_	+2.5° (neat)	*(S)-(Z)*
PL_	+2.5° (neat)	*(S)-(Z,Z)*
SS_	-2.91° ($CHCl_3$)	*(S)*
SO_	-2.8° ($CHCl_3$)	*(S)-(Z)*
OO_	-1.91° ($CHCl_3$)	*(S)-(Z,Z)*
OL_	-2.6° ($CHCl_3$)	*(R)-*(all Z)
LL_	-2.0° ($CHCl_3$)	*(S)*
LO_	-4.47°	*(R)-*(all Z)

Notes: * P-palmitic; S-stearic; O-oleic; L- linoleic.

triglycerides (including 15 chiral triglycerides) are found as the major constituents in palm oil (Jurriens, 1968). The major chiral triglycerides in palm oil are POO, POS, PPO, PLO, POL, SOO, SLP and PPS. The selected optical rotation of the isolable enantiomers are given in *Table 3* (Gunstone *et al*., 1994). The triacylation of glycerol by three dissimilar fatty acids brings about achiral and symmetrical triglycerides.

It is believed that the positional distribution of the fatty acids in the dietary triglycerides in palm oil play a crucial role in the metabolism and biological effects of these fatty acids. Moreover, the physiological and, eventually, the pathological effects of a dietary triglyceride depends not only on its fatty acid composition but also, possibly on its stereochemical configuration and positional isomerism (Renaud *et al*., 1995).

Phospholipids (phosphoglycerides)

Phospholipids are important metabolic intermediates. They are lipids containing phosphorus. All natural representatives of this group are diacyl derivatives of the *sn*-glycerol-3-phosphate. Their compositions are generally dependent on the origin of the lipids and the fatty acids pattern.

All of the phospholipids found in crude palm oil are chiral molecules (*Table 4*) irrespective of whether the two fatty acids acylated at *sn*-1 and *sn*-2 are the same or different (Gunstone *et al*., 1994). The moiety attached to the 3-phosphate could be derived from amine, alcohol or polyols. The major chiral phospholipids of palm oil are phosphatidylcholine (PtdCho), phosphatidylethanolamine (PtdEtn), phosphatidylinositol (PtdIns), phosphatidylglycerol (PtdGro), phosphatidic acid (PtdA) and phosphatidylserine (PtdSer).

Tocol

Tocols in palm oil consist of two series of compounds; tocopherols and tocotrienols. They are derived from chroman-6-ol with the side chains attached to C-2 of the heterocyclic ring. Tocopherol has a 16-C saturated isoprenoid side chain and possesses three asymmetric centres at C-2, C-4' and C-8', making possible four pairs of enantiomers. Tocotrienol has a 16-C triene isoprenoid unit with 2*R*, 3′-*E* and 7′-*E* configurations and exhibit chiral centres at C-2 and two pro-chiral centres at C-4′and C-8′. Depending on the methylation arrangement of the four nuclear positions in chroman-6-ol, it is possible to have four types of tocols. They are designated as α-, β-, γ- and δ-tocopherols and tocotrienols.

In palm oil, α-tocopherol, γ-tocopherol, α-tocotrienol, γ-tocotrienol and δ-tocotrienol are found available (Rossell *et al*., 1983). However, only the α-tocopherol (1, *Figure 1*); $[\alpha]_{546}$ –3.0° (benzene)[11] and the γ-tocopherol (2, *Figure 1*); $[\alpha]_D$ –2.4° (alcohol) (Budavari *et al*., 1989) are chiral. It is believed that vitamin E has the ability to protect patients against the side effects of some cancer treatment, such as radiation and chemotherapy treatments (Tolonen, 1990). Most of the commercial vitamin E capsules are derived from δ-α-tocopheryl acetate, $[\alpha]_D$ +3.2° (ethanol) which is 58% more biologically active than the *l*-form, $[\alpha]_D$ –2.0° (ethanol) (Budavari *et al*., 1989). Thus, the chirality factor plays a vital role in the performance of vitamin theraphy.

Carotenoids

The characteristic reddish colour of crude palm oil is caused by carotenoids. Alpha- and β-carotenes are the major components, with δ-carotene, γ-carotene, xanthophylls and lycopene present in minor quantities.

The chiral carotenoids in palm oil are α-carotene (3, *Figure 1*), $[\alpha]_{643}$ +385° (benzene) with 6′*R*-configuration and δ-carotene, $[\alpha]_D$ +352° (hexane) (Budavari *et al*., 1989). Although β-carotene (4, *Figure 1*) does not possess chiral value, it is the most important pro-vitamin A. It has biological functions such as protection against photosensitization, free radicals, lipid peroxidation, cancer and cataract (Mathews-Roth, 1982). In this content, the chirality feature is independent of its biological properties.

Sterols

The major sterols in palm oil are β-sitosterol (5, *Figure 1*), campesterol (6, *Figure 1*) and stigmasterol (7, *Figure 1*). They are optically active (*Table 5*) (Rossell *et al*., 1983).

They differ in the configuration of the linear chains attached to C-20. The chirality features of these compounds are not only similar to known natural products but also act as natural hypocholesterolic agents as well as intermediates to steroids (Goh *et al*., 1985).

TABLE 3. OPTICAL ROTATIONS OF TRIACYLGLYCEROLS (TG)

Type of fatty acid substituents*	Optical rotation, $[M]_{300}$ (solvent)	Configuration
PPO	-3.6° (C_6H_6)	*(S)-(Z)*
POO	-3.3° (C_6H_6)	*(S)-(Z,Z)*
SSO	+3.4° (C_6H_6)	*(R)-(Z)*

Notes: *P-palmitic; S-stearic; O-oleic.

TABLE 4. OPTICAL ROTATIONS OF PHOSPHOLIPIDS

Type of phospholipids*	Specific rotation, $[\alpha]_D$ (solvent)	Configuration
PPPtdCho	+7.0° ($CHCl_3$)	*(R)-L*
PPPtdEtn	+6.55°	*(R)*
PPPtdA	+4.0° ($CHCl_3$)	*(R)*
PPPtdSer	+5.5° ($CHCl_3$, MeOH/H_2O)	*(R)-L*
POPtdEtn	+6.35° ($CHCl_3$)	*(R)-(Z)*
POPtdIns	+6.1° ($CHCl_3$)	*(R)-D*
POPtdIns	+9.2° ($CHCl_3$)	*(R)-L*
POPtdIns (tri NH_4)	+1.8° ($CHCl_3$)	*(R)-DL*
POPtdA (di NH_4)	+4.5° ($CHCl_3$)	*(R)-(Z)*
PLPtdEtn	+6.0° ($CHCl_3$)	*(R)-*(all *Z)*
SSPtdCho	+6.2° ($CHCl_3$/MeOH)	*(R)*
SSPtdEtn	+6.2° ($CHCl_3$/AcOH)	*(R)*
SSPtdGro	+2.0° ($CHCl_3$)	*(R)*
SSPtdA	+3.8° ($CHCl_3$)	*(R)*
SSPtdSer	+7.4° ($CHCl_3$/Me_2CO)	*(R)-DL*
SOPtdCho	+6.0° ($CHCl_3$)	*(R)-(Z)*
SOPtdEtn	+6.0° ($CHCl_3$)	*(R)-(Z)*
SLPtdCho	+5.02°	*(R)-L-*(all *Z)*
OOPtdCho	+6.1° ($CHCl_3$/MeOH)	*(R)-(Z,Z)*
OOPtdEtn	+6.0° ($CHCl_3$)	*(R)-*(all *Z)*
OOPtdGro	+2.35° (EtOH)	*(*all *Z)*
OOPtdA	+3.8° ($CHCl_3$)	*(R)-(Z,Z)*
OOPtdSer	+21.3° (C_6H_6)	*(R)-D*
	-17.8° (C_6H_6)	*(R)-L*
	+4.9° (C_6H_6)	*(R)-DL*
OSPtdCho	+6.2° ($CHCl_3$)	*(R)-(Z)*
OSPtdEtn	+6.0° ($CHCl_3$)	*(R)-(Z)*
OLPtdEtn	+6.0° ($CHCl_3$)	*(R)-*(all *Z)*
OPPtdA	+2.05° ($CHCl_3$)	*(R)*
LLPtdCho	+6.02°	*(R)-L*
LLPtdEtn	+6.2° ($CHCl_3$)	*(R)-*(all *Z)*
LnPPtdEtn	+6.2° ($CHCl_3$)	*(R)-*(all *Z)*
LnLnPtdEtn	+6.1° ($CHCl_3$)	*(R)-*(all *Z)*
LnLnPtdA	+31.0° ($CHCl_3$)	*(R)-*(all *Z)*

Notes: *P-palmitic; S-stearic; O-oleic; L-linoleic; Ln-linolenic.

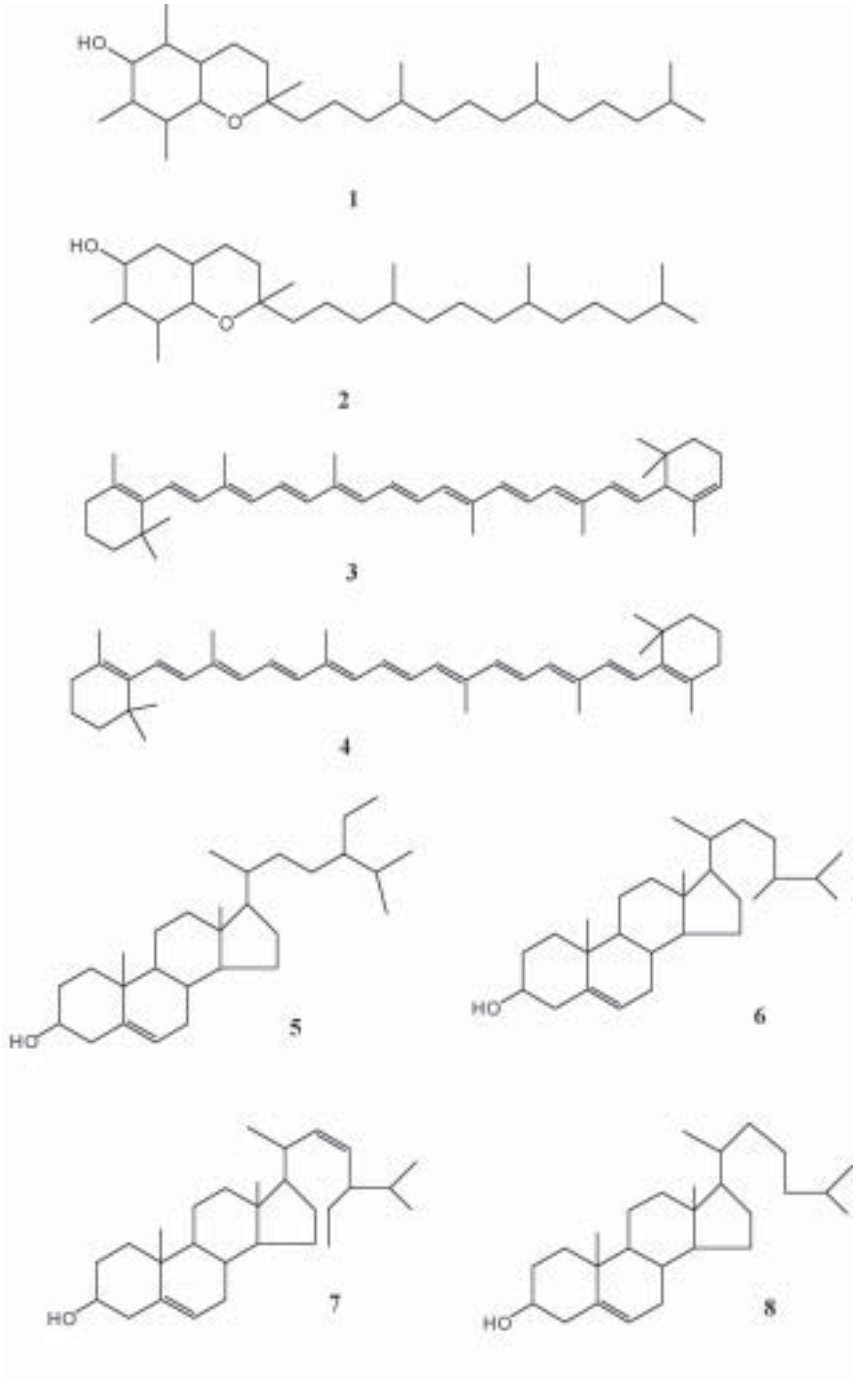

Figure 1. The structures of some palm-based chiral compounds.

TABLE 5. OPTICAL ROTATIONS OF STEROLS

Type of sterols	Specific rotation, $[\alpha]_D$ (solvent)	Positions of chiral carbon centres
β-Sitosterol	-37.0° ($CHCl_3$)	C-3, C-8, C-9, C-10, C-13, C-14, C-17, C-20
Campesterol	-33.0° ($CHCl_3$)	C-3, C-8, C-9, C-10, C-13, C-14, C-17, C-20, C-24
Stigmasterol	-51.0° ($CHCl_3$)	C-3, C-8, C-9, C-10, C-13, C-14, C-17, C-10, C-14
Cholesterol (8)	-39.5° ($CHCl_3$)	C-3, C-8, C-9, C-10, C-13, C-14, C-17, C-20

CONCLUSION

The present discussion of chirality in palm oil components is mainly meant to provide us with some basic information in this less explored field. Although most of the palm oil components exhibit chiral characteristics, they have been taken for granted. However, the chirality factors that effect biological activities have not been highlighted.

Sophisticated isolation and purification processes of individual compounds from a pool with a variety of chiral systems are now available. These have rendered the possibility of investigating and analysing chiral components of palm oil and their possible influence on metabolism in human diets. Consequently, stereochemical studies of chiral palm oil components present new research opportunities thus providing many challenging and interesting investigations.

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