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New Lignans from the Perisperm of *Sesamum indicum*

RAPHAEL GROUGNET,† PROKOPIOS MAGIATIS,† SOFIA MITAKU,† ARIS TERZIS,‡ FRANÇOIS TILLEQUIN,§ AND ALEXIOS-LEANDROS SKALTSOUNIS*,†

Division of Pharmacognosy and Natural Products Chemistry, Department of Pharmacy, University of Athens, Panepistimiopolis Zografou, GR-15771 Athens, Greece, X-ray Laboratory, NCSR DEMOKRITOS, Athens 15310, Greece, and Laboratoire de Pharmacognosie de l'Université René Descartes, UMR/CNRS 8638, Faculté de Pharmacie, 4 Avenue de l'Observatoire, F-75006 Paris, France

A procedure, based on XAD-4 adsorption resin, which permits the obtainment of enriched polyphenolic extracts from *Sesamum indicum* perisperm (coat) has been developed. Chemical analysis of the obtained extracts led to the identification of 16 lignans. Among them, two new lignans, (+)-saminol and (+)-episesaminone-9-*O*-β-D-sophoroside, have been isolated. Additionally, the relative stereochemistry of (-)-sesamolactol, previously reported as todolactol A epimer, has been unequivocally defined using X-ray crystallography. The structures of all new compounds were determined by spectroscopic methods, mainly by the concerted application of 1D and 2D NMR techniques (HMQC, HMBC, and NOESY) and mass spectroscopy.

KEYWORDS: ***Sesamum indicum*; perisperm; lignans; (+)-saminol; (+)-episesaminone-9-*O*-β-D-sophoroside; (−)-sesamolactol; XAD-4 resin adsorption**

INTRODUCTION

Sesame (*Sesamum indicum*, Pedaliaceae) is one of the most important oilseed crops. Worldwide production, which is currently increasing, reaches about 3.3 Mt annually. It is mainly cultivated in developing countries, particularly in Central America, Tropical Africa, and Eastern Asia (*1*). The interest in sesame oil arises from its high content of unsaturated fatty acids and antioxidant lignans, exemplified by sesamin, sesamolin, and sesaminol (*2*). The whole seed also possesses high-quality nutritional value, representing a good source of protein and trace elements. The process used by the food industry for the dehulling of sesame seeds produces huge quantities of sesame coat, which is an important agricultural waste. Sesame coat has been reported to exhibit significant antioxidant activity related to the presence of phenolic compounds (*3*−*5*). Nevertheless, it has never been previously studied from a chemical point of view.

Recent studies showed that several major complications could occur during and after long-term hormone replacement therapy (HRT), including the increased incidence of venous thromboembolism and breast cancer (*6*). Phytoestrogens, such as lignans, may constitute an alternative to HRT. In this context, the development of an efficient methodology for obtaining extracts enriched in lignans and polyphenols from sesame perisperm appeared highly desirable. The present work was undertaken to identify secondary metabolites contained in sesame seed coats, with a special emphasis on the methodology for obtaining enriched polyphenolic extracts.

MATERIALS AND METHODS

General Experimental Procedures. Optical rotations were measured with a Perkin-Elmer 341 polarimeter. The IR spectra were obtained on a Perkin-Elmer Paragon 500 instrument. NMR spectra were recorded on Bruker DRX 400 and Bruker AC 200 spectrometers [^{1}H (400 and 200 MHz) and ^{13}C (50 MHz)]; chemical shifts are expressed in ppm downfield from TMS. The ^{1}H−^{1}H and the ^{1}H−^{13}C NMR experiments were performed using standard Bruker microprograms. Electrospray mass spectra were recorded with a Q-Tof1 Micromass apparatus equipped with an ESI-Z spray source (ESI-MS; Vc = 30 V). Medium-pressure liquid chromatography (MPLC) was performed with a Büchi model 688 apparatus on columns containing Si gel 60 Merck (20−40 μm). Thin layer chromatography (TLC) was performed on plates coated with Si gel 60 F_{254} Merck, 0.25 mm. Resin adsorption experiments were performed using XAD-4 (Rohm and Haas).

Plant Material. Sesame perisperms were obtained during the industrial procedure of sesame dehulling from Haitoglou SA (Thessaloniki, Greece). The industrial dehulling procedure includes two steps: in a first step, the whole sesame grains are treated with water (40 °C) in order to facilitate the removal of the perisperm, and in a second step, the perisperm is removed and separated mechanically.

Extraction and Isolation. Dried ground perisperms of *Sesamum indicum* L. (15 kg) were exhaustively extracted at room temperature with solvents of increasing polarity: cyclohexane (3 × 8 L), CH_2Cl_2 (3 × 8 L), and MeOH (3 × 8 L). The dried methanol extract (0.850 kg) was diluted with water (5 L) and filtered. The precipitate A (380 g) contained major quantities of less polar (water-insoluble) lignans, free from sugars. The filtrate was passed through a column containing 0.7 kg of XAD-4 resin. The resin was rinsed with water (2 L). Elution

* To whom correspondence should be addressed. Tel.: +30-210-7274598. Fax: +30-210-7274594. E-mail: skaltsounis@pharm.uoa.gr.
† University of Athens.
‡ NCSR DEMOKRITOS.
§ Université René Descartes.

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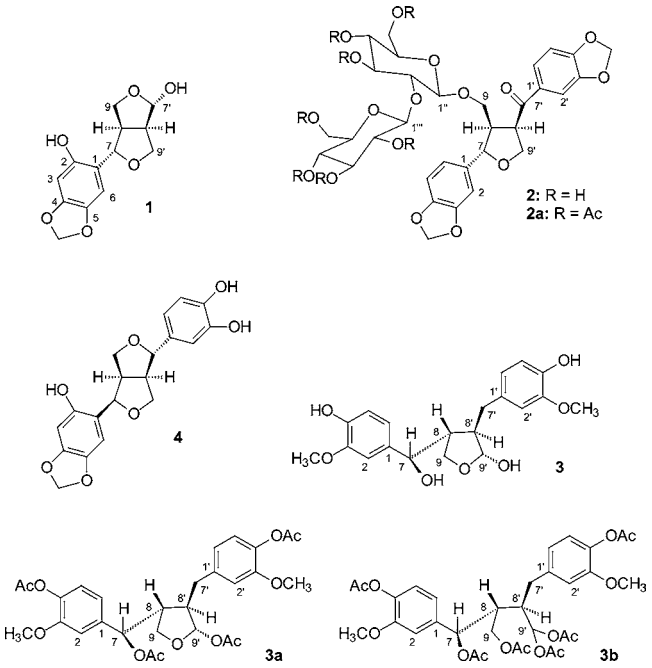

Figure 1. Structures of compounds **1**–**4**.

with MeOH (3 L) followed by evaporation under reduced pressure afforded an enriched polyphenolic extract B (65 g).

Repeated column chromatography performed on the precipitate A and the enriched polyphenolic extract B permitted the isolation of 16 lignans. Thirteen known compounds were identified on the basis of their physical and spectral data, in comparison with literature values. The structures of the new compounds were established using NMR spectroscopy and mass spectrometry (MS).

Column chromatography on silica gel 60 Merck (40−65 μm) of a portion of the water-insoluble precipitate A (20 g of 380 g), using a CH_2Cl_2/MeOH mixture of increasing polarity (from 100:0 to 0:100) gave 40 fractions of 500 mL. Fractions 16−19 (2.420 g) were rechromatographed on silica gel 60 Merck (40−65 μm) with cyclohexane/acetone (100:0 to 0:100 gradient), to afford successively (+)-sesamine (537 mg) (*7*), (+)-sesaminol (289 mg) (*8*), (+)-piperitol (12 mg) (*9*), (+)-episesaminone (57 mg) (*10*), (+)-pinoresinol (162 mg) (*11*), (−)-matairesinol (12 mg) (*12*), (+)-acuminatin (15 mg) (*13*), and (−)-7-hydroxymatairesinol (28 mg) (*14*).

A portion of the enriched polyphenolic extract B (22 g of 65 g) was submitted to chromatography on a column containing Si gel 60 Merck (40−65 μm), using a CH_2Cl_2/MeOH mixture of increasing polarity (from 100:0 to 0:100) to afford 40 fractions of 500 mL. Fractions 10−17 (2.546 g) were rechromatographed on silica gel 60 Merck (40−65 μm) with cyclohexane/acetone (80:20 to 0:100 gradient), to afford (+)-pinoresinol (243 mg) (*11*), (+)-saminol (12 mg) (**1**), (+)-lariciresinol (186 mg) (*15*), (+)-5′-methoxy-lariciresinol (10 mg) (*16*), (+)-episesaminol-6-catechol (16 mg) (*17*) (**4**), and (−)-sesamolactol (*18*, *19*) (94 mg) (**3**) (**Figure 1**). Fraction 35 (900 mg) was submitted to MPLC on R-18 silica gel, using a H_2O/MeOH gradient of decreasing polarity (from 100:0 to 0:100 gradient), to afford (+)-pinoresinol glucoside (21 mg) (*20*), (+)-episesaminone-9-*O*-β-D-sophoroside (78 mg) (**2**), and (+)-sesaminol diglucoside (66 mg) (*21*).

(+)-Saminol (1). White amorphous solid, $[\alpha]_D$ +30° ($CHCl_3$, *c* 0.2). ^{1}H NMR ($CDCl_3$): δ 3.01 (1H, *tdd*, *J* = 8, 5.5, 1 Hz, H-8), 3.09 (1H, *ddd*, *J* = 9, 8, 7.5 Hz, H-8′), 3.54 (1H, *dd*, *J* = 9, 7.5 Hz, H-9′a), 3.88 (1H, *dd*, *J* = 9, 1 Hz, H-9a), 4.15 (1H, *dd*, *J* = 9, 5.5 Hz, H-9b), 4.39 (1H, *d*, *J* = 8 Hz, H-7), 4.43 (1H, *t*, *J* = 9 Hz, H-9′b), 5.37 (1H, *br s*, H-7′), 5.88 (2H, *d*, O−CH_2−O), 6.44 (1H, *s*, H-6), 6.47 (1H, s, H-3). ^{13}C NMR ($CDCl_3$): δ 51.3 (C-8), 53.1 (C-8′), 68.6 (C-9), 71.3 (C-9′), 87.6 (C-7), 99.8 (C-3), 102.0 (O−CH_2−O), 102.5 (C-7′), 105.9 (C-6), 115.4 (C-1), 141.9 (C-5), 148.0 (C-4), 151.2 (C-2). HRESI-MS: *m*/*z* 289.0691 (calculated for $C_{13}H_{14}O_6Na$ 289.0688).

(+)-Episesaminone-9-*O*-β-D-sophoroside (2). Colorless prisms, mp 253 °C (acetone), $[\alpha]_D$ +20° (CH_3OH, *c* 0.2). IR (MeOH, CaF_2) cm^{-1}: 1648 (CO), 1604, 1504, 1409, 1250. ^{1}H NMR (CD_3OD): δ 2.83 (1H, *m*, H-8), 3.10−3.45 (8H, *overlapped*, H-2″, H-3″, H-4″, H-5″, H-2‴, H-3‴, H-4‴, H-5‴), 3.39 (1H, *overlapped*, H-9b), 3.57 (1H, *dd*, *J* = 12, 6 Hz, H-6‴a), 3.67 (1H, *dd*, *J* = 12, 5 Hz, H-6″a), 3.78 (2H, *overlapped*, H-6″b + H-6‴b), 3.87 (1H, *dd*, *J* = 10, 6.5 Hz, H-9a), 4.12 (1H, *d*, *J* = 7.5 Hz, H-1‴), 4.28 (3H, *m*, H-1″+ H-9′a + H-9′b), 4.43 (1H, *m*, H-8′), 4.87 (1H, *overlapped*, H-7), 5.97 (2H, *s*, O−CH_2−O), 6.09 (2H, *s*, O−CH_2−O), 6.81 (1H, *d*, *J* = 8 Hz, H-5), 6.92 (1H, *dd*, *J* = 8, 1.5 Hz, H-6), 6.94 (1H, *d*, *J* = 8 Hz, H-5′), 6.98 (1H, *d*, *J* = 1.5 Hz, H-2), 7.50 (1H, *d*, *J* = 1.5 Hz, H-2′), 7.72 (1H, *dd*, *J* = 8, 1.5 Hz, H-6′). ^{13}C NMR (CD_3OD): δ 47.1 (C-8′), 51.8 (C-8), 61.2 (C-6″, C-6‴), 66.1 (C-9), 69.8 (C-4″), 70.0 (C-4‴), 70.0 (C-9′), 74.8 (*C*2‴), 76.1 (C-3″, C-5″, C-3‴), 77.7 (C-5‴), 82.0 (C-2″), 83.2 (C-7), 101.0 (O−CH_2−O), 101.4 (C-1‴), 102.1 (O−CH_2−O), 104.1 (C-1″), 106.5 (C-2), 107.6 (C-5′), 107.7 (C-2′), 107.8 (C-5), 119.9 (C-6), 125.2 (C-6′), 132.1 (C-1′), 135.5 (C-1), 147.3 (C-3), 147.8 (C-4), 148.4 (C-3′), 152.3 (C-4′), 198.5 (C-7′). HRESI-MS: *m*/*z* 717.2112 (calculated for $C_{32}H_{38}O_{17}Na$ 717.2109).

(+)-Episesaminone-9-*O*-β-D-sophoroside Heptaacetate (2a). An ice-cooled mixture of acetic anhydride (0.5 mL) and dry pyridine (0.5 mL) was added to **2** (10 mg). After the resulting mixture was stirred at room temperature for 48 h, the solvents were removed by evaporation under reduced pressure, to afford **6** (6 mg) as an amorphous pale yellowish solid, $[\alpha]_D$ +32° (CH_3OH, *c* 0.2). ^{1}H NMR (CD_3OD): δ 1.95−2.05 (21H, *s*, CH_3CO), 2.76 (1H, *quintet*, *J* = 7.0 Hz, H-8), 3.39 (1H, *dd*, *J* = 9, 8 Hz, H-2″), 3.52 (1H, *dd*, *J* = 10, 7 Hz, H-9b), 3.65 (1H, *ddd*, *J* = 9, 2.5, 2 Hz, H-5″), 3.78 (1H, *ddd*, *J* = 9, 4, 2 Hz, H-5‴), 3.83 (1H, *dd*, *J* = 10, 7 Hz, H-9a), 3.95 (1H, *dd*, *J* = 11.5, 2.5 Hz, H-6″b), 4.08 (1H, *dd*, *J* = 11.5, 2 Hz, H-6″a), 4.10 (1H, *overlapped*, H-6‴a), 4.28 (2H, *overlapped*, H-9′a + H-9′b), 4.30 (1H, *d*, *J* = 8 Hz, H-1″), 4.36 (1H, *dd*, *J* = 8, 7 Hz, H-8′), 4.42 (1H, *dd*, *J* = 12, 4 Hz, H-6‴b), 4.58 (1H, *overlapped*, H-1‴), 4.76 (1H, *t*, *J* = 9 Hz, H-4″), 4.93 (1H, *overlapped*, H-7), 5.03 (1H, *t*, *J* = 9 Hz, H-4‴), 5.07 (1H, *t*, *J* = 9 Hz, H-3″), 5.13 (1H, *t*, *J* = 9 Hz, H-3‴), 5.13 (1H, *t*, *J* = 9 Hz, H-2‴), 5.96 (2H, *s*, O−CH_2−O), 6.11 (2H, *s*, O−CH_2−O), 6.82 (1H, *d*, *J* = 8 Hz, H-5), 6.92 (1H, *dd*, *J* = 8, 1.5 Hz, H-6), 6.98 (1H, *d*, *J* = 1.5 Hz, H-2), 6.99 (1H, *d*, *J* = 8 Hz, H-5′), 7.51 (1H, *d*, *J* = 1.5 Hz, H-2′), 7.69 (1H, *dd*, *J* = 8, 1.5 Hz, H-6′). ^{13}C NMR (CD_3OD): δ 19.1−19.6 (*C*H_3CO), 47.8 (C-8′), 51.6 (C-8), 61.4 (C-6″), 61.9 (C-6‴), 66.1 (C-9), 67.9 (C-4‴), 68.8 (C-4″), 69.9 (C-9′), 71.1 (C-5″), 71.3 (C-5‴), 73.1 (C-3″), 73.7 (*C*2‴), 78.2 (C-2″), 82.4 (C-7), 100.2 (C-1‴), 100.7 (C-1″), 100.7 (O−CH_2−O), 102.1 (O−CH_2−O), 105.9 (C-2), 107.3 (C-2′), 107.6 (C-5′), 107.4 (C-5), 119.8 (C-6), 124.2 (C-6′), 131.6 (C-1′), 135.4 (C-1), 147.1 (C-4), 148.1 (C-3), 148.5 (C-3′), 152.6 (C-4′), 169.1−171.2 (*C*H_3CO), 197.8 (C-7′). HRESI-MS: *m*/*z* 1011.2741 (calculated for $C_{46}H_{52}O_{24}Na$ 1011.2746).

(−)-Sesamolactol (3). Colorless prisms, mp 168 °C, $[\alpha]_D$ −35° (CH_3OH, *c* 0.2). ^{1}H NMR (CD_3OD): δ 2.38 (2H, *m*, H-8, H-8′), 2.45 (1H, *dd*, *J* = 13, 8 Hz, H-7′a), 2.58 (1H, *dd*, *J* = 13, 7 Hz, H-7′b), 3.75 (3H, *s*, O−CH_3), 3.77 (3H, *s*, O−CH_3), 3.85 (1H, *dd*, *J* = 8.5, 6.5 Hz, H-9a), 3.96 (1H, *t*, *J* = 8.5 Hz, H-9b), 4.63 (1H, *d*, *J* = 5 Hz, H-7), 5.04 (1H, *br. s*, H-9′), 6.46 (1H, *dd*, *J* = 8, 2 Hz, H-6′), 6.51 (1H, *d*, *J* = 2 Hz, H-2′), 6.63 (1H, *d*, *J* = 8 Hz, H-5′), 6.69 (1H, *dd*, *J* = 7, 2 Hz, H-6), 6.69 (1H, *d*, *J* = 7 Hz, H-5), 6.70 (1H, *d*, *J* = 2 Hz, H-2). ^{13}C NMR (CD_3OD): δ 36.9 (C-7′), 47.7 (C-8), 48.2 (C-8′), 52.9 (O−*C*H_3), 53.0 (O−*C*H_3), 66.5 (C-9), 71.6 (C-7), 99.8 (C-9′), 107.0 (C-2), 109.9 (C-2′), 112.1 (C-5), 112.3 (C-5′), 116.0 (C-6), 119.1 (C-6′), 128.9 (C-1′), 133.0 (C-1), 142.0 (C-4′), 142.9 (C-4), 145.2 (C-3), 145.7 (C-3′). HRESI-MS: *m*/*z* 399.1420 (calculated for $C_{20}H_{24}O_7Na$ 399.1419).

Crystal Data of 3. $C_{20}H_{24}O_7$, M_r = 376.39; μ = 0.105 mm^{-1}, d_x = 1.384 g cm^{-3}, $P2_1$, *Z* = 4, *a* = 13.127 Å (*5*), *b* = 10.148 Å (*4*), *c* = 13.588 (*5*) Å, β = 93.90 (*1*)°, *V* = 1805.9 (*12*) Å^3.

X-ray Diffraction. Slow crystallization from acetone yielded colorless prismatic crystals. A crystal with approximate dimensions 0.25 × 0.35 × 0.50 mm was mounted in air and covered with epoxy glue. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo Kα radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11° < 2θ < 23°. Intensity data were recorded using a θ−2θ scan to $2\theta_{max}$ = 50°, with a scan speed of 5.0°/min and scan range 1.6 plus $\alpha_1\alpha_2$

separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization corrections were applied using Crystal Logic software. Symmetry equivalent data were averaged with $R_{int} = 0.0143$ to give 5298 independent reflections from a total of 5520 collected. The structure was solved by direct methods using SHELXS-86 (*22*) and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 (*23*) using 5289 reflections and refining 675 parameters. All hydrogen atoms were located by difference maps and were refined isotropically. All non-hydrogen atoms were refined anisotropically. The final values for R1, wR2, and GOF for all data are 0.0486, 0.1028, and 1.028, respectively. The maximum and minimum residual peaks in the final difference map were 0.177 and −0.235 e/Å. The largest shift/esd in the final cycle was 0.011. Crystallographic data, excluding stucture factors, have been deposited at the Cambridge Crystallographic Data Centre under the deposition number CCDC 602945. Copies can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-0-1223-226033; e-mail: deposit@ccdc.cam.ac.uk).

(+)-Episesaminol-6-catechol (4). Yellow amorphous solid, $[\alpha]_D$ +53° (CH_3OH, *c* 0.2). ^1H NMR (acetone-d_6): δ 3.01 (2H, *m*, H-8, H-8′), 3.81 (1H, *dd*, *J* = 9, 5 Hz, H-9$_{ax.}$), 3.94 (1H, *dd*, *J* = 9, 4 Hz, H-9′$_{ax.}$), 4.14 (1H, *dd*, *J* = 9, 7 Hz, H-9$_{eq.}$), 4.28 (1H, *dd*, *J* = 9, 7 Hz, H-9′$_{eq.}$), 4.62 (1H, *d*, *J* = 5 Hz, H-7′), 4.92 (1H, *d*, *J* = 5 Hz, H-7), 5.88 (2H, *m*, O−C*H*$_2$−O), 6.44 (1H, *s*, H-3), 6.70 (1H, *dd*, *J* = 8, 2 Hz, H-6′), 6.78 (1H, *d*, *J* = 8 Hz, H-5′), 6.81 (1H, *s*, H-6), 6.86 (1H, *d*, *J* = 2 Hz, H-2′), 7.86 (1H, exch. D_2O, OH-3′), 7.88 (1H, exch. D_2O, OH-4′), 8.32 (1H, exch. D_2O, OH-2). ^{13}C NMR (acetone-d_6): δ 55.5 (C-8, C-8′), 73.2 (C-9′), 73.4 (C-9), 85.6 (C-7), 86.2 (C-7′), 98.7 (C-3), 101.5 (O−*C*H$_2$−O), 106.2 (C-6), 114.6 (C-2′), 116.5 (C-5′), 119.3 (C-6′), 121.8 (C-1), 134.9 (C-1′), 142.5 (C-5), 146.2 (C-4′), 147.1 (C-3′), 149.0 (C-4), 150.9 (C-2). Other data identical to those previously published (*17*).

RESULTS AND DISCUSSION

The basic target of this study was the development of a methodology for obtaining enriched polyphenolic extracts from the sesame perisperm. The first step in this procedure was the extraction with cyclohexane and CH_2Cl_2 in order to remove efficiently the contained oil (about 20%).

In a second step, the plant material was extracted with methanol and the dried extract was diluted in water. The solution was filtered, giving precipitate A, and the filtrate was submitted to an adsorption process on XAD-4 resin in order to enrich the polyphenol concentration. The chemical structure of the resin material favors the adsorption by weak interactions of molecules with moieties of high electron density, such as aromatic rings. In contrast, sugars or polar lipids cannot establish this kind of interaction and are eluted with the water flow during the rinsing phase. Finally, the polyphenolic compounds were recovered by elution with MeOH, giving an enriched extract B.

The total procedure (**Figure 2**) afforded two kinds of mixtures: on one hand, the precipitate A, containing the less polar polyphenols, and on the other hand, extract B, containing the water-soluble polyphenols. It is noticeable that both extracts are almost free from sugars and polar lipids, which where successfully removed by application of the adsorption resin methodology.

The extracts obtained were submitted to several chromatographic separations affording several known and three new lignans, (+)-saminol (**1**), (+)-episesaminone-9-*O*-β-D-sophoroside (**2**), and (-)-sesamolactol (**3**).

Compound **1** was obtained as a colorless amorphous solid, whose molecular formula was determined as $C_{13}H_{14}O_6$ by HRESI-MS. The ^1H NMR spectrum recorded in $CDCl_3$ exhibited a broad singlet at δ 5.37 and a doublet at δ 4.39 (*J* = 8 Hz) characteristic of the H-7 and H-7′ of sesamolinol-type lignans. The presence of only two aromatic protons and three

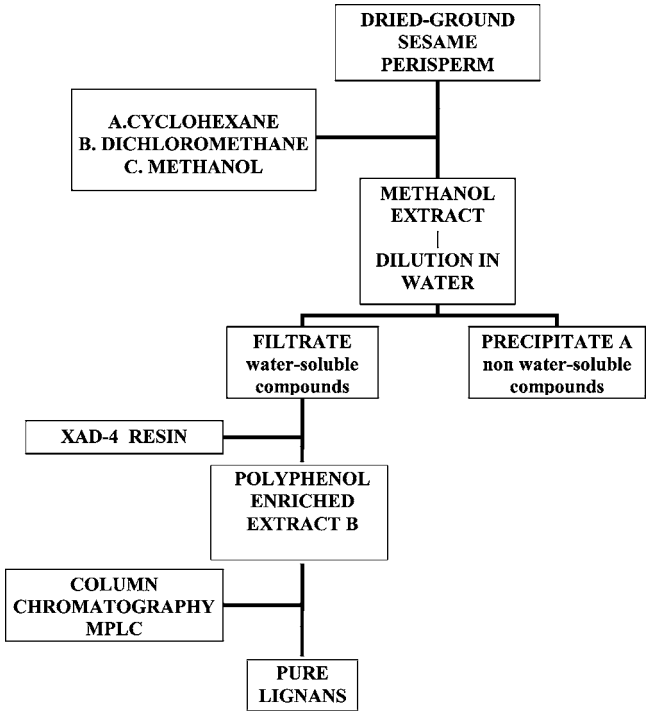

Figure 2. Schematic overview of the procedure for obtaining enriched polyphenolic extracts from the sesame perisperm.

oxygenated aromatic carbons in combination with the observed molecular weight indicated that the compound contained only one aromatic ring. Other signals accounted for two aliphatic methynes (H-8, H-8′), two oxygenated methylenes (H-9, H-9′), and one methylenedioxy group. The above signals were closely related to those previously described for samin (*24*), both in terms of chemical shifts and coupling constants. The only noticeable difference was the presence of an additional aromatic hydroxy group. Its position was deduced from the HMBC correlation of H-7 with C-2, permitting the structure of compound **1** to be determined as 2-hydroxysamin, for which we propose the name saminol.

Compound **2** was obtained as colorless prisms, with molecular formula $C_{32}H_{38}O_{17}$ determined by HRESI-MS. Prominent fragment ions observed at *m*/*z* 555 and 203, on one hand, and 365, on the other hand, were strongly suggestive of the presence of one episesaminone and two hexosyl units. Comparison of the NMR data with those of episesaminone revealed that **2** was a 9-*O*-diglycoside of episesaminone. The identification of the sugars as two β-glucopyranoses was deduced from a thorough study of the ^1H and ^{13}C NMR signals of **2** and its peracetyl derivative **2a**. Of particular interest were the doublets typical for the anomeric protons, observed at δ 4.30 (*J* = 8 Hz) in the ^1H NMR spectrum of **2a** for H-1″ and 4.12 (*J* = 7.5 Hz) in that of **2** for H-1‴. The nature of the sugar units were further confirmed and the position of the interglycosidic linkage deduced from the COSY spectrum of **2a**, in which the anomeric H-1″ proton signal correlated with that of H-2″, whose strong shielding at 3.39 ppm indicated that the oxygen atom at position 2″ was not acetylated but attached to the second sugar unit (*25*). Furthermore, the ^{13}C NMR signals attributable to the glycosidic moieties of compound **2** were essentially similar to those previously published for β-sophorose itself and various β-D-sophorosides (*25*−*27*). Finally, prolonged enzymatic hydrolysis of **2** with β-D-glucosidase afforded, although in low yield, (+)-episesaminone, (*10*), confirming the structure of **2** as (+)-episesaminone-9-*O*-β-D-sophoroside.

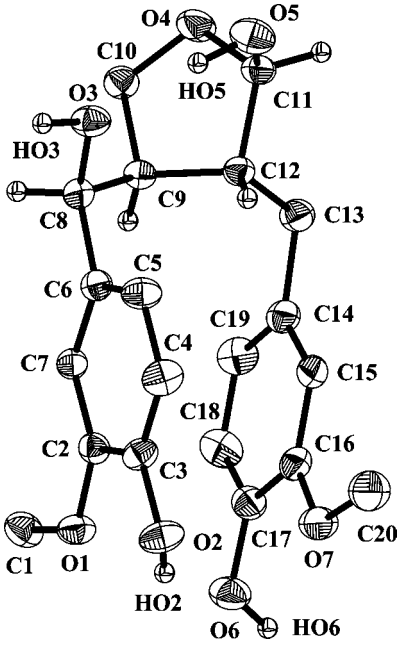

Figure 3. Labeled ORTEP plot (Oak Ridge Thermal Ellipsoid Plot) of **3** with ellipsoids drawn at the 40% probability level. Only the critical hydrogen atoms are shown.

Compound **3** was identified as a 3,4-dibenzyltetrahydrofuran-2-ol derivative. In 1982, Miller et al. (*18*) described the isolation and structure determination of the peracetylated form of a similar compound named isoliovil, whose stereochemistry was not elucidated. Later, in 1988, Ozawa and Sasaya (*19*) described the isolation of a similar compound, named todolactol A, which was also studied as its peracetylated derivative. In this paper, the name todolactol A was assigned to a mixture of epimers at position 7. No clear explanation was given as to why the epimers involved the benzylic carbon 7 and not the lactol carbon 9′, as in the case of todolactol B (*19*). Also, the assignment of each epimer to the corresponding NMR data was not definitely established. In our hands acetylation of the natural compound **3** gave two products: **3a** and **3b**. The first one, **3a**, corresponding to the peracetylated form of **3,** presented ^{1}H NMR, ^{13}C NMR, and optical rotation data almost identical to those previously published for one of the two epimers of todolactol A (*19*) and isoliovil tetraacetate (*18*). Nevertheless, significant differences were noticed in the multiplicities of the H-9′ signal in ^{1}H NMR spectroscopy between **3a** (br. s), and isoliovil tetraacetate (d, $J = 7$ Hz). The second acetylation product **3b** presented ^{1}H and ^{13}C NMR data closely related to those of the product to which the structure of the second epimer of todolactol A had been assigned (*19*). A thorough study of the ^{1}H and ^{13}C NMR spectra revealed that **3b** was not an epimer of **3a**, but possessed an open ring structure, which was further confirmed by a diagnostic correlation between H-9 and $COCH_3$ in the HMBC spectrum. In order to define unequivocally the relative stereochemistry of **3**, we performed a single-crystal X-ray diffraction analysis and found that the asymmetric centers should be depicted as 7*S**, 8*R**, 8′*R**, and 9′*R**. A three-dimensional view of the structure is given in **Figure 3**. To avoid any confusion with the previously reported structures of isoliovil and todolactol A, we propose the name sesamolactol for **3**.

Finally, compound **4** was identified as episesaminol-6-catechol. This compound presented identical spectroscopic data (*17*) with a biotranformation product of sesaminol glucoside by a specific type of *Aspergillus*. This is the first report of the isolation of this compound as a naturally occurring product.

In summary, the use of XAD-4 adsorption resin permits an efficient enrichment of polyphenolic extracts from *Sesamum indicum* perisperm. Two new lignans, (+)-saminol (**1**) and (+)-episesaminone-9-*O*-β-D-sophoroside (**2**), have been isolated from the extracts. The relative stereochemistry of a third lignan, (−)-sesamolactol (**3**), has been unequivocally defined by X-ray crystallography.

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