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Revisão

The Styracaceae

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RESUMO: "Styracaceae". Styracaceae possui 11 gêneros e aproximadamente 160 espécies, sendo árvores e arbustos, distribuídos nas regiões tropicais e subtropicais. Esta família é conhecida principalmente devido ao gênero *Styrax*, que é notório pela produção de um material resinoso, produto patológico, coletado a partir de incisões realizadas no caule. Esta goma é usada em perfumes, como anti-séptico, expectorante, incenso e material fumegante. Este artigo reúne os estudos fitoquímicos e biológicos realizados em 11 espécies desta família. Foram consultados 92 artigos e levantadas 130 substâncias, que indicaram que *Styrax* é o maior gênero desta família e o único que foi extensivamente investigado.

Unitermos: Styracaceae, *Styrax*, lignanas, tritepenenos, revisão.

ABSTRACT: The Styracaceae contains 11 genera and approximately 160 species consisting of small trees and shrubs, mostly native to tropical and subtropical regions. This family is well-known by the genus *Styrax*, which is notorious due to the production of resinous material, a pathological product, harvested by making incisions into the tree's bark. The gum is used in perfumes, as antiseptic, expectorant, incense, and fumigating material. This paper reviews the phytochemical and biological studies carried out on 11 species of this family. A total of 92 papers were consulted, and 130 compounds were described, thus these data indicate that *Styrax* is by far the largest genus in the family, and the only which has been extensively investigated.

Keywords: Styracaceae, *Styrax*, lignans, tritepenes, review.

INTRODUCTION

The Styracaceae contains approximately 160 species grouped in 11 genera: *Styrax* L., *Halesia* J. Ellis ex L. (three species), *Alniphyllum* Matsum. (three species), *Bruinsmia* Boer. & Koord. (two species), *Huodendron* Rehder (four species), *Parastyrax* W. W. Sm. (two species), *Pterostyrax* Siebold & Zucc. (four species), *Rehderodendron* Hu (five species), *Changiostyrax* C. T. Chen (one specie), *Melliodendron* Hand. –Mazz. (one specie), and *Sinojackia* Hu (five species) (Fritsch et al., 2001). Traditionally, the Styracaceae has been placed with some or all of the following families: Ebenaceae, Lissocarpaceae, Sapotaceae, and Symplocaceae at the ordinal level Ebenales (Cronquist, 1981). *Styrax* is, by far, the largest genus in the family, consisting of about 130 species, which comprises 80 % of the total number of species in Styracaceae. This genus has a widespread but disjunctive distribution, occurring in the Americas, eastern Asia, and the Mediterranean region, with over half the species presented in South America (Fritsch, 2001). *Styrax* distinguishes among other genera of this family due to the production of resinous material, commonly referred to as benzoin resin, usually secreted when sharp objects injure the bark. This resin has been used in many parts of the world in perfumery, cosmetics, and folk medicine as expectorant and in inhalation (Costa, 1996; Corrêa, 1926). The tincture of benzoin (a mixture of 10% Benzoin, 2% Aloe, 8% Storax, 4% Tolu Balsam and alcohol) has a long history of use and can be traced back to at least the 15th century in the medical uses, and Egyptian and Greek times as a balsam (Lovell, 1993). It has both fungicidal and bacteriostatic properties, and it also adheres well to skin and mucous membranes (Hjorth, 1961). It has been used added to water and glycerine in preparing steam inhalations for bronchitis, asthma and other respiratory disorders (Steiner; Leifer, 1949). Allergy for tincture of Benzoin was firstly reported in 1874 with a patient who developed a purpuric eruption after inhaling its vapors. On the other hand, there have been few reports of contact allergy to Benzoin tincture suggesting that it is in fact not a strong sensitizer (Scardamaglia et al., 2003). In this review the biological activities and phytochemistry of *Styrax* are considered, since this genus is the only studied extensively.

MATERIAL AND METHODS

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The keywords used for this review were Styracaceae, *Styrax*, *Halesia*, *Alniphyllum*, *Bruinsmia*, *Huodendron*, *Parastyrax*, *Pterostyrax*, *Rehderodendron*, *Changiostyrax*, *Melliodendron*, and *Sinojackia*, and the search was realized using Chemical Abstracts, Web of Science and PubMed.

RESULTS AND DISCUSSION

Consultation of the references found in our search resulted in the elaboration of a list of species studied. Table 1 and 2 describe the biological activities of crude extracts and fractions and the distribution of the compounds isolated by species, respectively. The compounds structures are presented in Figures 1-5, and the references correspond to the first report on that compound or the one in which the most relevant spectroscopic data were presented.

Bioactivity of crude extracts and fractions

The resin gum benzoin from *S. benzoin* inhibited LDL (low-density lipoproteins) oxidation lower than 2% (Teissedre; Waterhouse, 2000), and the insaponifiable fraction, obtained from the balsamic resin, showed immune stimulant activity, stimulating the phagocytic activity of reticulum endothelial system in mice inoculated with *Escherichia coli* (Delaveau et al., 1980).

Oral administration of dry 70 % ethanolic extract from the stems of *S. camporum* Pohl , known in Brazil as "estoraque do campo" or "cuia do brejo", to rats during 15 days decreased the ulceration size, gastric secretion volume, and increased collagen fibre number of chronic ulcer induced by acetic acid. It was established that the ethyl acetate fraction was responsible for the antiulcer activity. This study supported the use of *S. camporum* hydroalcoholic extract in folk medicine as antiulcer drug (Bacchi; Sertié, 1994, Bacchi et al., 1995).

The crude extract of the leaves of *S. ferrugineus* showed antibacterial and antifungal activities against *Staphylococcus aureus*, *Candida albicans*, and *Cladosporium sphaerospermum*, and the MIC (minimum inhibition concentration) was established as 200 μg/mL, 800 μg/mL, and 750 μg, respectively (Pauletti et al., 2000).

The 70% aqueous acetone extract of *S. formosanum* was evaluated by various antioxidant assays, including the free radical scavenging ability using 1,1-diphenyl-2-picrylhydrazyl (DPPH), hydroxyl radicals, and reducing power assays. This extract showed IC_{50} of 31.5 μg/mL and 0.3 μg/mL in the DPPH and hydroxyl radicals assays, respectively. The total phenolic content was determined as 2.7 mg of gallic acid/g of dried extract determined according to a Folin-Ciocalteu method. In the reducing power assay the activity was moderated, and the results obtained in the different antioxidant assays, did not show significant correlations (Hou et al., 2003).

In Japan, pericarps of *S. japonica* found use as washing soap, cough medicine and as a piscicidal agent (Takanashi, 1991). The propan-2-one extract of *S. japonica* and the water insoluble fraction showed insecticidal action against *Culex pipiens* larvae (Yamaguchi et al. 1950), and the essential oil exhibited strong growth inhibitory effects on *Bacillus cereus*, *Salmonella typhimurium* and *S. aureus* (Kim; Shin, 2004; Kim et al., 2004c). The hexane and dichloromethane soluble fractions obtained from the methanolic extract of the seeds exhibited strong cytotoxic activities in brine shrimp lethality test (Kwon; Kim, 2002). A methylene chloride soluble fraction from the methanolic extract of the stem bark showed significant cell cytotoxicity *in vitro* by SRB method against five human tumor cell lines A549 (non small cell lungcarcinoma), SK-OV-3 (adenocarcinoma, ovary malignant ascites), SK-MEL-2 (malignant melanoma, metastasis to skin of thigh), MES-AS (uterine sarcoma), and HCT-15 (colon adenocarcinoma) (Kim et al., 2004b), and exhibited significant MMP-1 expression inhibition *in vitro* (Moon et al., 2005b). In addition, total saponins extract increased plasma ACTH (adrenocorticotropic hormone), corticosterone and glucose after the intraperitoneal administration in rats **(**Yokoyama et al., 1982).

The methanolic extract of *S. obassia* was found to inhibit production of inflammatory mediators, such as prostaglandins and leukotrienes, *in vitro* assay system (Jung et al., 2003).

Gummy exudates of *S. officinalis* could be applied as a suspending agent for the formulation of antiacid preparations (Shahjahan; Islan, 1998), and pericarps have been used as fish poison, furthermore it has been claimed that saponins appeared to be responsible for the ichthyotoxic action, also they were highly haemolytic (Segal et al., 1964, 1966). As well, the aqueous ethanolic extract from the aerial parts showed antitumoral activity against 3PS test systems (141 % in 10 mg/kg doses), but were toxic in high doses (Ulubelen; Gören, 1973). Proestos and coworkers studied extracts by HPLC/UV and distinguished, identified, to quantify phenolic compounds. They also determined the antioxidant capacity with the Rancimat test using sun flower oil as substrate, and the total phenolic content in the extracts applying the Folin-Ciocalteu assay. Among the plants investigated was the leaves of *S. officinalis* that showed total phenolic concentration of 18.4 ± 0.3 mg of gallic acid/g of dry extract, and the antioxidant protection factor was equal to 1.8 to the ground material and 1.7 to the methanolic extract. Additionally, the methanolic extract showed slight antimicrobial activity against *E. coli*, *B. cereus* and *Pseudomonas putida*, the susceptibility of the test organisms to the extract was determined by employing the standard disk diffusion technique (Proestos et al. 2006).

Essential oil from the wood of *S. tonkinensis* was investigated by disk diffusion assay and the broth dilution method against *Aspergillus niger* and *A. flavus*. It showed

Table 1. Biological activity of crude extracts and fractions.

Species	Biological Activity	References
S. benzoin	Antioxidant	Teissedre; Waterhouse, 2000
	Immune stimulant activity	Delaveau et al., 1980
S. camporum	Antiulcer	Bacchi; Sertié, 1994, Bacchi et al., 1995
S. ferrugineus	Antibacterial and antifungal	Pauletti et al., 2000
S. formosanum	Antioxidant	Hou et al., 2003
S. japonica	Insecticidal	Yamaguchi et al., 1950
	Antibacterial	Kim; Shin, 2004; Kim et al., 2004c
	UV protection	Moon et al., 2005b
	Cytotoxicity	Kwon; Kim, 2002; Kim et al., 2004b
	Increase: ACTH, corticosterone and glucose	Yokoyama et al., 1982
	Angiotensin converting enzyme	Barbosa-Filho et al., 2006
S. obassia	Antiinflammatory	Jung et al., 2003
S. officinalis	Suspending agent	Shahjahan; Islan, 1998
	Haemolytic	Segal et al., 1966
	Antitumoral activity	Ulubelen; Goren, 1973
	Antioxidant and antimicrobial	Proestos et al., 2006
S. tonkinensis	Antifungic	Shin, 2003
	Immune stimulant activity	Delaveau et al., 1980

relatively small inhibition zones of 4 mm and 5 mm at 25 mg/disk, respectively. The MIC was 0.78 mg/mL for both species of *Aspergillus* (Shin, 2003). Additionally, the balsamic resin and its insaponifiable fraction stimulated the phagocytic activity of reticulum endothelial system in mice inoculated with *E. coli* (Delaveau et al., 1980). The importance of this plant promoted its inclusion in Brazilian Pharmacopoeia (Brandão et al., 2006).

Bioactivity of metabolites

The saponins, jegosaponin A-D (**1-4**) led to complete suppression of the sensation of sweetness induced by 0.2 M sucrose, but did not suppress the sweetness of 0.4 M sucrose at 1 mM solution (Yoshikawa et al., 2000).

Saponin A-B (**5-6**) showed fungistatic activity against *Rhizoctonia solani*, *Pytium aphanidermatum*, *Rhizopus mucco*, *A. niger*, *Fusarium oxyporumlycopersici* and *Trichoderma viride*. For the first two fungi, no mycelial growth inhibition was detected for **5** at concentrations lower than 80 μg/mL. The dose response for 50 % inhibition (ID_{50}) for **5** was determined for *T. viride*, *R. mucco*, *F. oxysporum*, and *A. niger* as 3.4 μg/mL, 25 μg/mL, 11.7 μg/mL, and 12 μg/mL, respectively. Saponin **6** had no fungistatic activity at lower than 80 μg/mL except on *T. viride*. The mechanism of action of saponins was related to their hemolytic activity (Zehavi et al., 1986; Segal et al., 1966).

Egonol (**7**), homoegonol (**8**), egonol-β-glucoside (**9**), homoegonol-β-glucoside (**10**), and dihydrodehydrodiconiferyl alcohol (**11**) showed antibacterial and antifungal activities against *S. aureus* and *C. albicans* with MIC in the range 10 - 20 μg/mL, respectively. However, only **7** and **8** were active in the range of 5 - 10 μg to *C. sphaerospermum* (Pauletti et al., 2000).

Egonol (**7**), homoegonol (**8**), and syringaresinol (**12**) were evaluated for their cytotoxicity by the MTT method in three cell lines: Hep-2 (larynx epidermoid carcinoma), HeLa (human cervix carcinoma) and C6 (rat glioma). Moderate activities had been observed for **7** against C6 (10.5 μM/mL), and Hep-2 (11.8 μM/mL), also for **8** against HeLa (16.5 μM/mL). Nevertheless, **12** was less active showing a range 27.9- 82.6 μM/mL (Teles et al., 2005). Additionally, the egonol derivatives attracted the attention of synthetic chemists due to its activity against human leukemic HL-60 cells (Hirano et al., 1994).

A lignan, pinoresinol (**13**), is useful as an antioxidant for thermoplastic resins, foods, pharmaceuticals, and cosmetics, and also as an antihypertensive (Kakie et al., 1994).

The compounds styraxlignolide B-F (**14-18**), taraxerol (**19**), syringin (**20**), and pinoresinol glucoside (**21**) were tested *in vitro* for antioxidant activity against DPPH. Compounds **15**, **16**, **17** and **21** exhibited weak radical-scavenging activity, with IC_{50} values of 380, 278, 194, and 260 μM, respectively. In contrast, **14**, **18**, **19** e **20** which do not have free phenolic groups at all showed IC_{50} > 500 μM (Min et al., 2004a).

Compounds egonol-β-glucoside (**9**), styraxjaponoside A-B (**22-23**), matairesinoside (**24**), and dihydrodehydrodiconiferyl alcohol-9'-*O*-glucoside (**25**) showed no cytotoxicity against the human dermal fibroblasts in the test dose 0.1 – 10 μM, when compared

Table 2. Species and organ source distribution of compounds.

Species	Source	Compounds	References
S. americana	seeds oil	**7**	Hopkins et al., 1967
S. benzoin	resin	**13**, **42**, **43**, **80-83**, **87-89**, **93-96**, **99-101**	Pastorova et al., 1997; Djerassi et al., 1955; Schroeder, 1968; Reinitzer, 1914, 1921
S. camporum	leaves	**71**, **73**, **74**, **76-79**	Pauletti et al., 2002
	steams	**7**, **8**, **12**	Teles et al., 2005
	trunk's bark	**8**, **97**, **98**, **81**, **110**	Giesbrecht et al., 1985
S. ferrugineus	leaves	**7-11**, **44**, **76**, **110**, **111**	Pauletti et al., 2000
S. formosanum	fruits	**7**, **9**	Schreiber; Stevenson, 1976; Kawai; Sugimoto, 1940
S. japonica	fruits/ pericarps	**1-4**, **7**, **46**, **52**, **53**, **59**, **69**, **75**	Yoshikawa et al., 2000; Nakano et al., 1967a, b, 1969; Kitagawa et al., 1974a, b, 1975, 1980; Sugiyama et al., 1967a, b, Takanashi; Takizawa, 1988b
	kernel	**124-126**, **130**	Breuer et al., 1987
	leaves	**13**, **45**, **115-118**	Kakie et al., 1994; Kim; Shim, 2004
	seeds	**7**, **54**, **58-60**, **124-127**	Kwon; Kim, 2002; Okada, 1915
	steam bark	**7**, **9**, **14-29**, **32-35**	Kim et al., 2004a, b; Min et al., 2004a, b
S. obassia	bark	**55**, **61**, **62**, **68**	Kinoshita et al., 2005
	fruit	**114**	Asahina, 1908
	seeds	**7**, **9**, **29**, **54**, **58-60**	Takanashi; Takizawa, 1988a, b, 2002; Takanashi et al., 1974
S. officinalis	fruits	**114**	Anil, 1977
	leaves	**70**, **83-86**, **90-92**, **106-110**, **113**, **119-123**	Ulubelen; Gören, 1973; Ulubelen et al., 1978; Ulubelen, 1976; Proestos et al., 2006
	pericarps	**5**, **6**, **47-51**	Segal et al., 1964; Zehavi et al., 1986; Yayla et al., 2002; Anil, 1979
	seeds	**7-9**, **54-59**, **66**, **67**, **72**, **124-130**	Akgul; Anil, 2003a, b; Anil, 1980; Segal et al., 1967; Ulubelen et al., 1976
S. parallelo neurum	resin	**13**, **80-83**, **87-89**, **93-96**, **99-101**	Pastorova et al., 1997; Nitta et al., 1984
S. perkinsiae	seeds	**7**, **9**, **30**, **31**, **54-56**, **59**, **63-65**, **110**, **112**	Li et al., 2005
S. tonkinensis	essential oil	**80**, **98**, **102**	Shin, 2003
	resin	**36-44**, **80**, **81**, **87**, **93-95**, **99**, **103-105**	Reynolds, 1982; Schroeder, 1968; Reinitzer, 1914, 1921; Huang, 1999; Wang et al., 2006a,b

to the control. Therefore the effect of compounds on the expression of type I procollagen, and the MMP-1 proteins (matrix metalloproteinases) in cultured human dermal fibroblasts was examined, and **23** increased the type I procollagen protein expression level by 518.9 ± 18.0%, and decreased the MMP-1 protein expression level significantly by an average of 62.1 ± 8.3 % at 10 μM, compared with the vehicle-treated controls cells. The UV induced MMP-1 protein expression level was significantly inhibited by 63.5 ± 17.6 %, at the same concentration by a pretreatment with **23** in the cultured human dermal fibroblasts. Compound **23** exhibited almost equivalent effects on type I procolagen and MMP-1 expression to that of epigallocatechin-3-gallate, which is used as a positive control. These results indicated that **23** can be used for the treatment and prevention of the skin aging processes (Kim et al., 2004a).

Compounds egonol (**7**), styraxlignolide A (**26**), styraxoside A-B (**27-28**), and masutakeside (**29**) were tested for anti-complement activity of the complement system; the modulation of complementary activity should be beneficial in the therapy of inflammatory diseases. Compounds **7**, **26**, **28**, and **29** inhibited the hemolytic activity of the complement system with IC_{50} values of 33, 123, 65, and 166 μM, respectively. In addition to, compound **27** was unable to inhibiting complement activity. The hydrolytic analogues of **26** and **28** were inactive showing that sugar moiety is necessary to enhance the anti-complementary activity of human serum against erythrocytes. On the other hand, the methylenedioxy group seems to be important to the inhibition (Min et al., 2004b).

The benzofurans 5-(3′′-hydroxypropyl)-7-hydroxy-2-(3′,4′-methylenedioxyphenyl)benzofuran (**30**), and *trans*-5-(3′′′-hydroxypropyl)-7-methoxy-2[2′,3′-dihydro-3′-hydroxymethyl-7′-methoxy-2′-(3′′-methoxy-4′′-hydroxyphenyl)-benzofuran-5′-yl]benzofuran (**31**) exhibited cytotoxic activity *in vitro* using two breast cancer cell lines MCF-7 and MDA-MB-231 (Li et al., 2005).

The triterpenes, oleanolic aldehyde acetate (**32**), erythrodiol-3-acetate (**33**), euphorginol (**34**), and anhydrosophoradiol-3-acetate (**35**) were evaluated for their cytotoxicity against tumor cells lines. Compounds **32** and **35** exhibited potent cytotoxicity against A549, SK-OV-3, SK-MEL-2, MES-AS, and HCT-15, which IC_{50} were in the range 5.07 - 9.86 μg/mL, and 3.42 - 7.81 μg/mL, respectively (Kim et al., 2004b). Additionally, the compounds **32** and **35** exhibited potent cytotoxicity against human dermal fibroblasts (IC_{50} 0.84 μM and 1.12 μM, respectively), and compounds **33** and **34** did not showed cytotoxicity against human dermal fibroblasts in the test dose 0.01-1 μM. Thus the effect on the expression of metaloproteinases (MMP-1) and type I procollagem of **33** and **34** were examined in cultured human skin fibroblasts, given that the regulation mechanisms of MMPs activities are closely related to chronic skin diseases, such as melanona as well as photoaging, which showed higher MMP protein expression, and are caused by long term and repeated exposure of ultraviolet light. Thus **34** did not showed activity on the MMP-1 and type I procollagen synthesis, and **33** reduced the expression of MMP-1 but not MMP-2, at the mRNA and protein levels in a dose-dependent manner by UV irradiation, so it suggests that **33** plays an important role in the reduction of MMP-1 induction by UV irradiation and induced of type I procollagen (Moon et al., 2005a, b).

The triterpenoids, 3β-hydroxy-12-oxo-13Hα-olean-28,19β-olide (**36**), 6β-hydroxy-3-oxo-11α,12α-epoxyolean-28,13β-olide (**37**), 3β,6β-dihydroxy-11-oxo-olean-12-en-28-oic acid (**38**), 3β,6β-dihydroxy-11α,12α-epoxyolean-28,13β-olide (**39**), 19α-hydroxy-3-oxo-olean-12-en-28-oic acid (**40**), 6β-hydroxy-3-oxo-olean-12-en-28-oic acid (**41**), sumaresinolic acid (**42**), siaresinolic acid (**43**), and oleanolic acid (**44**) inhibited HL-60 cell growth with IG_{50} values ranging from 8.9 to 99.4 μM. Oleanolic acid (**44**) was the most effective antiproliferative agent, with an IG_{50} value of 8.9 μM, while (**39**) exhibited the least effective growth inhibition among these triterpenoids, it induced HL-60 cells to undergo differentiation as measured by an NBT reduction assay (Wang et al., 2006a).

Nerol (**45**) showed growth inhibitory effect in cooked rice package in the range of 0.5 - 1.5 log CFU/g, the result suggested that this compound could be used as potential agent to extend shelf life of cooked rice (Kim et al., 2004c).

Phytochemistry

Styrax has attracted considerable interest mainly due to the water insoluble resin that has been used in folk medicine and perfumery. Early works focused on the analyses of resin quality and possible adulterations. This resin, known as Benzoin gum, consists of several unique aromatic compounds. Among the resins preparation, the most important are the Siam Benzoin, which is produced from the barks of *S. tonkinense* and *S. benzoin*, and Sumatra Benzoin, obtained from *S. paralleloneurum* (Pastorova et al., 1997).

The phytochemistry investigation on this genus increased in 1915, when Okada isolated egonol (**7**) for the first time, as an unsaponifiable constituent of the seed oil of *S. japonica* and its structure was determined by Kawai and Sugiyama (Okada, 1915; Kawai; Sugiyama, 1939).

Other important classes of compounds, the saponins and sapogenin have been studied since 1899, when Keimatsu isolated jegosaponin from the fruits of *S. japonica*. Since then, the elucidation of the chemical structure of this saponin has been the subject of a number of investigations (Asahina; Momoya, 1914a, b, Sone, 1934, 1936, Tobinaga, 1958). However, in spite of these intensive studies, no structure could be proposed for this saponin until the years 1967 and 1969 (Nakano et al.,

1967, 1969). The earlier workers (Asahina; Momoya, 1914a, b; Sone, 1934, 1936; Tobinaga, 1958) reported that the acid hydrolysis of jegosaponin yielded 2 equivalents each of glucuronic acid and glucose (Matsunami, 1927) as well as a sapogenin which, on digestion with alkali, was hydrolyzed to tiglic acid and jegosapogenol (**46**) (Nakano et al., 1967). Actually, the jegosaponin isolated from *S. japonica* comprises several saponins, in which, the aglycones are the acylated (acetyl, tigloyl, or 2'-*cis*-hexenoyl) derivatives of **46**, and jegosapogenin is the major acid-hydrolysis product (Hayashi et al., 1967).

Besides, only one paper reported a comparative study between *Styrax* and *Halesia*. The seed, kernel or fruit oils of *S. japonicum* and *H. carolina* were analyzed for fatty acid composition, in *Halesia*, linoleic acid predominates over oleic acid, whereas in *Styrax*, equal amounts of these two acids are found (Breuer et al., 1987).

CONCLUSION

These data reveal predominately the occurrence of shikimate derivatives such as lignans derivatives of 3,7-dioxabicyclo [3.3.0], butanolide, and tetrahydrofuran, neolignans derivatives of dihydrobenzofuran, norlignans derivatives of benzofuran, phenylpropanoids, and phenolic acids, as well as the presence of acetate derivatives pentacyclic saponins and triterpenes in *Styrax* species. Some of saponins exhibited antisweet activity (**1**-**4**), fungistatic activity (**5**-**6**), and anti-inflammatory activity (**28**). The shikimate derivatives showed a variety of activities such as antibacterial and antifungal (**7**-**11**), cytotoxicity against tumor cell lines (**7**, **8**, **12**, **30**, **31**), antioxidant activity (**13**, **15**-**17**, **21**) antihypertensive (**13**), antiinflamatory (**7**, **26**, **28**, **29**), and prevention of skin aging process (**23**). The triterpenes showed cytotoxicity against tumor cell lines (**32**-**44**) and protection against UV irradiation (**33**). Our contribution was principally in relation to the isolation of pentacyclic triterpenes, and biological activity studies. Nevertheless, only some genera have been studied chemically, and the chemotaxonomic aspects of Styracaceae are far from being established. Otherwise it seems that *Styrax* accumulates norlignans derivatives as benzofuran, and it is important to point out that this particular class of norlignan occurs widely in *Styrax*. Thus benzofuran derivatives should be considered chemosystematic markers of *Styrax*. Additionally, it seems that *Styrax* being these derivatives leads chemistry. On the other hand, some extracts showed important activities and they might be useful as phytomedicines. *Styrax* has proven to be a very valuable genus to the discovery and utilization of medicinal natural products, and to drug discorery particularly lignans, norlignans, saponins and pentacyclic triterpenes.

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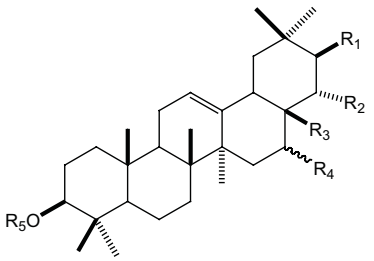


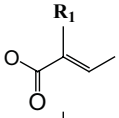
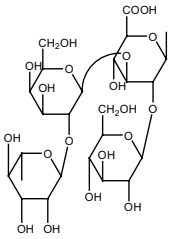
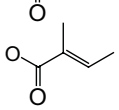
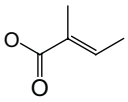
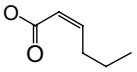
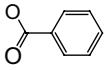
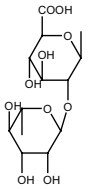
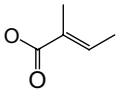
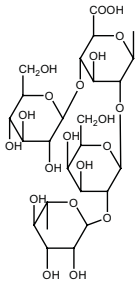
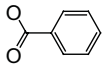
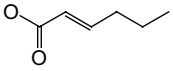
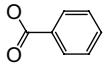
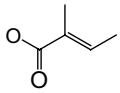
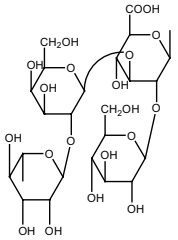
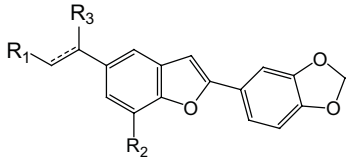
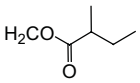
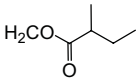
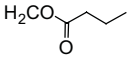
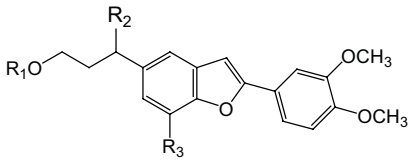
	R_1	R_2	R_3	R_4	R_5	Ref.
(**1**) Jegosaponin A		OAc	CH_2OH	α–OH		Yoshikawa et al., 2000
(**2**) Jegosaponin B		OH	CH_2OAc	α–OH		Yoshikawa et al., 2000
(**3**) Jegosaponin C	OH		CH_2OAc	α–OH		Yoshikawa et al., 2000
(**4**) Jegosaponin D		OH	CH_2OAc	α–OH		Yoshikawa et al., 2000
(**5**) Saponin A		OH	CH_2OH	α–OH	Glycosyl moiety	Segal et al., 1964; Zehavi et al., 1986
(**6**) Saponin B	OH	OH	CH_2OH	α–OH	Glycosyl moiety	Segal et al., 1964; Zehavi et al., 1986
(**28**) Styraxoside B	H_2	H_2	OH	=O		Min et al., 2004b
(**46**) Jegosapogenol, Barringtogenol C, or Jegosapogenol A	OH	OH	CH_2OH	α–OH	H	Nakano et al., 1967a, b, 1969
(**47**) Styrax-saponin A		OAc	CH_2OH	α–OH		Yayla et al., 2002
(**48**) Styrax-saponin B		OAc	CH_2OH	α–OH		Yayla et al., 2002
(**49**) Styrax-saponin C		OAc	CH_2OH	α–OH		Yayla et al., 2002
(**50**) Styrax-deacylsaponin	OH	OH	CH_2OH	α–OH		Yayla et al., 2002
(**51**) 21-Benzoyl-barringtogenol C		OH	CH_2OH	α–OH	H	Anil, 1979
(**52**) 21-Tigloyl-barringtogenol C		OH	CH_2OH	α-OH	H	Hayashi et al., 1967
(**53**) Deacyl-jegosaponin	OH	OH	CH_2OH	α–OH		Kitagawa et al., 1974a, b, 1975, 1980

Figure 1. Saponins from *Styrax* species

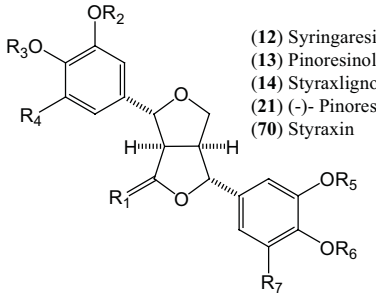


	R_1	R_2	R_3		Ref.
(**7**) Egonol	CH_2OH	OCH_3	H	2",3" dihydro	Pauletti et al., 2000
(**9**) Egonol-β-glucoside	CH_2O-Glucose	OCH_3	H	2",3" dihydro	Takanashi; Takizawa, 1988a
(**29**) Masutakeside I	Xylose-(1→6)-CH_2O-Glucose	OCH_3	H	2",3" dihydro	Min et al., 2004b
(**30**)5-(3"-Hydroxypropyl)-7-hydroxy-2-(3',4'-methylenedioxyphenyl)benzofuran	CH_2OH	OH	H	2",3" dihydro	Li et al., 2005
(**54**) Egonol acetate	CH_2OAc	OCH_3	H	2",3" dihydro	Akgul; Anil, 2003b
(**55**) Egonol-β-gentiobioside	CH_2O-Gentiobiosyl	OCH_3	H	2",3" dihydro	Anil, 1980
(**56**) Egonol-β-gentiotrioside	CH_2O-Gentiotriosyl	OCH_3	H	2",3" dihydro	Anil, 1980
(**57**) 5-(3"-Benzoyloxypropyl)-7-methoxy-2-(3',4'-methylenedioxyphenyl)benzofuran	CH_2O-Bezoyl	OCH_3	H	2",3" dihydro	Akgul; Anil, 2003b
(**58**) Egonol 2-methylbutanoato		OCH_3	H	2",3" dihydro	Takanashi; Takizawa, 1988a
(**59**) Demethoxy egonol	CH_2OH	H	H	2",3" dihydro	Takanashi et al., 1974
(**60**) Demethoxy egonol 2-methylbutanoato		H	H	2",3" dihydro	Takanashi; Takizawa, 1988a
(**61**) Obassioside B	CH_2O-Glucose	OCH_3	OH	2",3" dihydro	Kinoshita et al., 2005
(**62**) Obassioside C	Xylose-(1→6)-CH_2O-Glucose	OCH_3	OH	2",3" dihydro	Kinoshita et al., 2005
(**63**) 5-(3"-Butanoyloxypropyl)-7-methoxy-2-(3',4'-methylenedioxyphenyl)benzofuran		OCH_3	H	2",3" dihydro	Li et al., 2005
(**64**) Demethoxyegonol acetate	CH_2OAc	H	H	2",3" dihydro	Li et al., 2005
(**65**) (*E*)-5-(2"-formyl-vinyl)-7-methoxy-2-(3',4'-methylenedioxyphenyl)benzofuran	CHO	OCH_3	H	$\triangle^{2"}$	Li et al., 2005

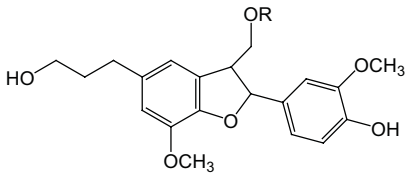


	R_1	R_2	R_3	Ref.
(**8**) Homoegonol	H	H	OCH_3	Pauletti et al., 2000
(**10**) Homoegonol-β-glucoside	Glucosyl	H	OCH_3	Pauletti et al., 2000
(**26**) Styraxlignolide A	Xylose-(1→6)-glucose	H	OCH_3	Min et al., 2004b
(**66**) Homoegonol-β-gentiobioside	Gentiobiosyl	H	OCH_3	Anil, 1980
(**67**) 5-[3"-(2-Methylbutanoyloxy)propyl]-7-methoxy-2-(3',4'dimethoxyphenyl)benzofuran		H	OCH_3	Akgul; Anil, 2003a
(**68**) Obassioside A	Glucosyl	OH	OCH_3	Kinoshita et al., 2005
(**69**) Demethoxyhomoegonol	H	H	H	Takanashi; Takizawa, 1988b

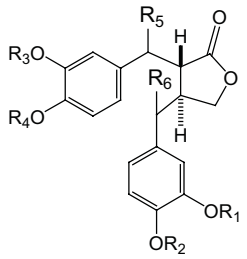
Figure 2. Lignans from *Styrax* species



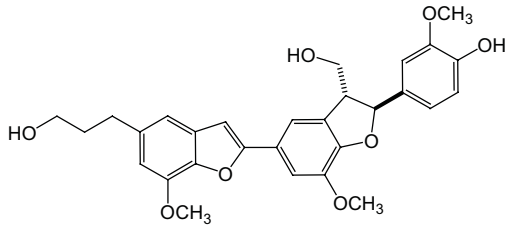
	R_1	R_2	R_3	R_4	R_5	R_6	R_7	Ref.
(**12**) Syringaresinol	H_2	CH_3	H	OCH_3	CH_3	H	OCH_3	Teles et al., 2005
(**13**) Pinoresinol	H_2	CH_3	H	H	CH_3	H	H	Kakie et al., 1994
(**14**) Styraxlignolide B	O	CH_3	Glc	H	$-CH_2-$		H	Min et al., 2004a
(**21**) (-)- Pinoresinol glucoside	H_2	CH_3	Glc	H	CH_3	H	H	Min et al., 2004a
(**70**) Styraxin	O	CH_3	H	H	$-CH_2-$		H	Ulubelen et al., 1978



	R	Ref.
(**11**) Dihydrodehydrodiconiferyl alcohol	H	Pauletti et al., 2000
(**25**) Dihydrodehydrodiconiferyl alcohol -9'-*O*-glucoside	Glc	Kim et al., 2004a

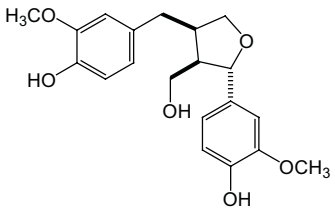


	R_1	R_2	R_3	R_4	R_5	R_6	Ref.
(**15**) Styraxlignoide C	CH_3	Glc	H	CH_3	H	H	Min et al., 2004a
(**16**) Styraxlignoide D	CH_3	Glc	CH_3	H	H	H	Min et al., 2004a
(**17**) Styraxlignoide E	CH_3	H	CH_3	Glc	H	H	Min et al., 2004a
(**18**) Styraxlignoide F	CH_3	Glc	CH_3	CH_3	H	H	Min et al., 2004a
(**22**) Styraxjaponoside A	$-CH_2-$		CH_3	Glc	OH	OH	Kim et al., 2004a
(**23**) Styraxjaponoside B	CH_3	Glc	CH_3	CH_3	H	H	Kim et al., 2004a
(**24**) Matairesinoside	CH_3	H	CH_3	Glc	H	H	Kim et al., 2004a



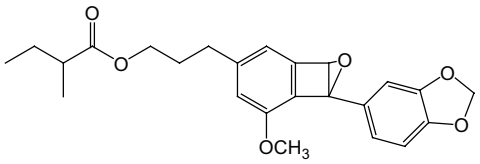
(**31**) *Trans*-5-(3'''-hydroxypropyl)-7-methoxy-2[2',3'-dihydro-3'-hydroxymethyl-7'-methoxy-2'-(3''-methoxy-4''-hydroxyphenyl)- benzofuran-5'-yl] benzofuran

Ref.
Li et al., 2005



(**71**) Lariciresinol

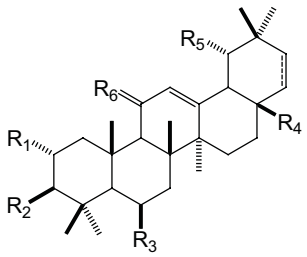
Ref.
Pauletti et al., 2002



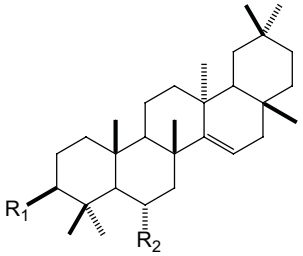
(**72**) 4-[3''-(1c-Methylbutanoyloxy)propyl]-2-methoxy-(3',4'-methylenedioxyphenyl)-1a, 5b-dihydrobenzo-[3,4]-cyclobutaoxirene

Ref.
Akgul; Anil, 2003b

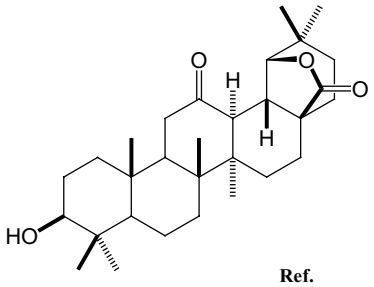
Figure 2. Contd.



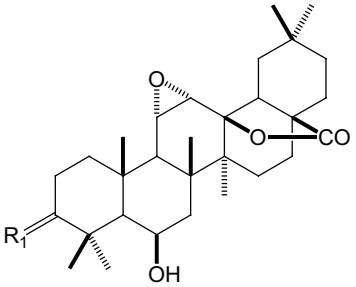
	R_1	R_2	R_3	R_4	R_5	R_6		Ref.
(**32**) Oleanolic aldehyde acetate	H	$OCOCH_3$	H	CHO	H	H_2	21,22 dihydro	Kim et al., 2004b
(**33**) Erythrodiol-3-acetate	H	$OCOCH_3$	H	CH_2OH	H	H_2	21,22 dihydro	Kim et al., 2004b
(**35**) Anhydrosophoradiol-3-acetate	H	$OCOCH_3$	H	CH_3	H	H_2	Δ^{21}	Kim et al., 2004b
(**38**) 3β,6β-Dihydroxy-11-oxo-olean-12-en-28-oic acid	H	OH	OH	COOH	H	O	21,22 dihydro	Wang et al., 2006a
(**40**)19α-Hydroxy-3-oxo-olean-12-en-28-oic acid	H	=O	H	COOH	OH	H_2	21,22 dihydro	Wang et al., 2006a
(**41**) 6β-Hydroxy-3-oxo-olean-12-en- 28-oic acid	H	=O	OH	COOH	H	H_2	21,22 dihydro	Wang et al., 2006a
(**42**) Sumaresinolic acid	H	OH	OH	COOH	H	H_2	21,22 dihydro	Djerassi et al., 1955
(**43**) Siaresinolic acid	H	OH	H	COOH	OH	H_2	21,22 dihydro	Reynolds, 1982
(**44**) Oleanolic acid	H	OH	H	COOH	H	H_2	21,22 dihydro	Pauletti et al., 2000
(**73**) Erythrodiol	H	OH	H	CH_2OH	H	H_2	21,22 dihydro	Pauletti et al., 2002
(**74**) 3β -O-*Trans-p*-coumaroy maslinic acid	OH	*O*-coumaroyl	H	COOH	H	H_2	21,22 dihydro	Pauletti et al., 2002



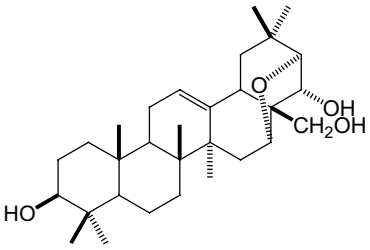
	R_1	R_2	Ref.
(**19**) Taraxerol	OH	H	Mim et al., 2004a
(**34**) Euphorginol	H	OH	Kin et al., 2004b



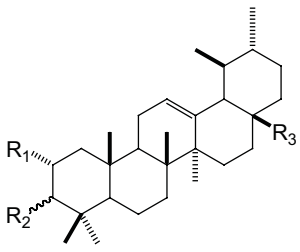
	Ref.
(**36**) 3β–Hydroxy-12-oxo-13Hα-olean-28,19β-olide	Wang et al., 2006a



	R_1	Ref.
(**37**) 6β-Hydroxy-3-oxo-11α,12α-epoxyolean-28,13β-olide	O	Wang et al., 2006a
(**39**)3β,6β-Dihydroxy-11α,12α-epoxyolean-28,13β-olide	β-OH, α-H	Wang et al., 2006a

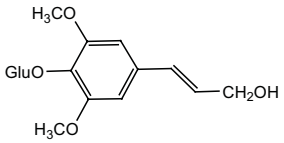


	Ref.
(**75**) Jegosapogenol B or Barringtogenol D	Sugiyama et al., 1967a, b

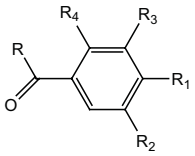


	R_1	R_2	R_3	Ref.
(**76**) Ursolic acid	H	β-OH	COOH	Pauletti et al., 2000
(**77**) 2α ,3α -Dihydroxy-urs-12-en-28-oic acid	OH	α-OH	COOH	Pauletti et al., 2002
(**78**) Uvaol	H	β-OH	CH_2OH	Pauletti et al., 2002
(**79**) 3β-O-*Trans-p*-coumaroyl-2α-hydroxy-urs-12-en-28-oic acid	OH	β-*O*-coumaroyl	COOH	Pauletti et al., 2002

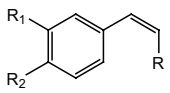
Figure 3. Triterpenes from *Styrax* species



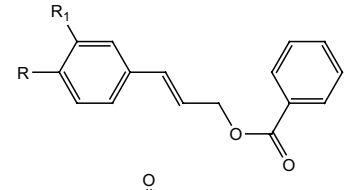
	Ref.
(**20**) Syrigin	Min B-S et al., 2004a



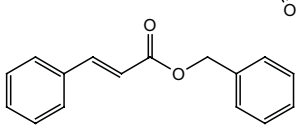
	R	R_1	R_2	R_3	R_4	Ref.
(**80**) Benzoic acid	OH	H	H	H	H	Schroeder, 1968
(**81**) Vanilin	H	OH	OCH_3	H	H	Schroeder, 1968
(**82**) *p*-Hydroxy benzaldehyde	H	OH	H	H	H	Pastorova et al., 1997
(**83**) Vanilic acid	OH	OH	OCH_3	H	H	Pastorova et al., 1997
(**84**) Gallic acid	OH	OH	OH	OH	H	Proestos et al., 2006
(**85**) Gentisic acid	OH	H	OH	H	OH	Proestos et al., 2006
(**86**)*p*-Hydroxy benzoic acid	OH	OH	H	H	H	Proestos et al., 2006



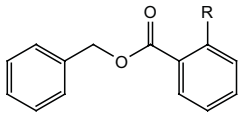
	R	R_1	R_2	Ref.
(**87**) Cinnamic acid	COOH	H	H	Reinitzer, 1914
(**88**) Coniferyl alcohol	CH_2OH	OCH_3	OH	Pastorova et al., 1997
(**89**) *p*-Coumaryl alcohol	CH_2OH	H	OH	Pastorova et al., 1997
(**90**) Caffeic acid	COOH	OH	OH	Proestos et al., 2006
(**91**) *p*-Coumaric acid	COOH	H	OH	Proestos et al., 2006
(**92**) Ferulic acid	COOH	OCH_3	OH	Proestos et al., 2006



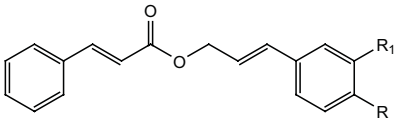
	R	R_1	Ref.
(**93**) Cinnamyl benzoate	H	H	Reinitzer, 1914
(**94**) *p*-Coumaryl benzoate	OH	H	Schroeder, 1968
(**95**) Coniferyl benzoate	OH	OCH_3	Reinitzer, 1914



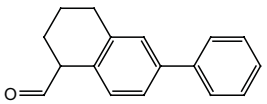
	Ref.
(**96**) Benzyl cinnamate	Pastorova et al., 1997



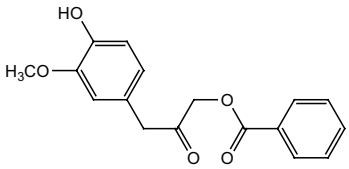
	R	Ref.
(**97**) Benzyl salicylate	OH	Giesbrecht et al., 1985
(**98**) Benzyl benzoate	H	Giesbrecht et al., 1985



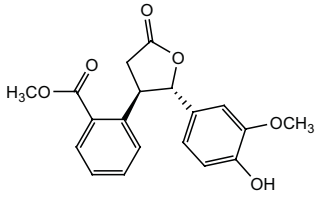
	R	R_1	Ref.
(**99**) Cinnamyl cinnamate	H	H	Pastorova et al., 1997
(**100**) *p*-Coumaryl cinnamate	OH	H	Pastorova et al., 1997
(**101**) Coniferyl cinnamate	OH	OCH_3	Pastorova et al., 1997



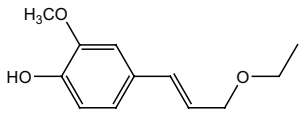
	Ref.
(**102**) 6-Phenyl-tetrahydro-naphthaline	Shin, 2003



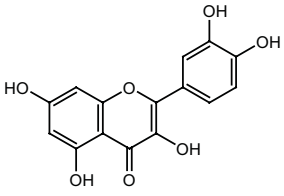
	Ref.
(**103**)3-(4-Hydroxy-3-methoxyphenyl)-2-oxopropyl benzoate	Wang et al., 2006b



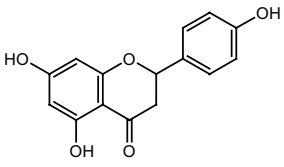
	Ref.
(**104**) *Trans* -(tetrahydro-2-(4-hydroxy-3-methoxyphenyl)-5-oxofuran-3-yl)methyl benzoate	Wang et al., 2006b



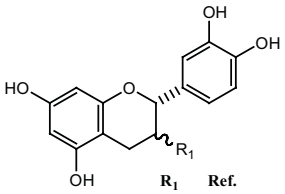
	Ref.
(**105**) 4-((*E*)-3-ethoxyprop-1-enyl)-2-methoxyphenol	Wang et al., 2006b



	Ref.
(**106**) Quercetin	Proestos et al., 2006

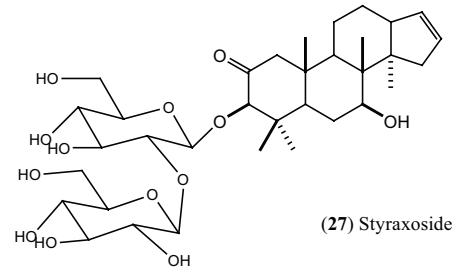


	Ref.
(**107**) Naringenin	Proestos et al., 2006

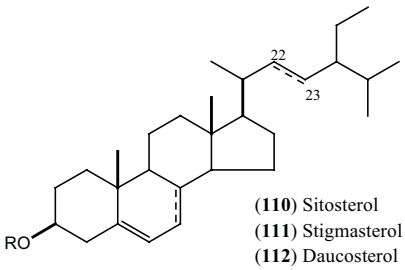


	R_1	Ref.
(**108**) Catechin	β-OH	Proestos et al., 2006
(**109**) Epicatechin	α-OH	Proestos et al., 2006

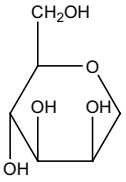
Figure 4. Phenolic compounds from *Styrax* species



(**27**) Styraxoside A — **Ref.** Min et al., 2004b



	R			Ref.
(**110**) Sitosterol	H	7,8 dihydro	22,23 dihydro	Ulubelen; Goren, 1973
(**111**) Stigmasterol	H	7,8 dihydro	Δ^{22}	Pauletti et al., 2000
(**112**) Daucosterol	Glc	7,8 dihydro	Δ^{22}	Li et al., 2005
(**113**) Δ^{7}-stigmasteryl-3-β-D-glucoside	Glc	Δ^{7}	22,23 dihydro	Ulubelen, 1976



(**114**) Styracitol or Styracite — **Ref.** Anil, 1977

		Ref.
(**45**) Nerol	$(CH_3)_2C=CH(CH_2)_2CH_3C=CHCH_2OH$	Kim; Shim, 2004
(**115**) *Trans*-2-heptenal	$CH_3(CH_2)_3CH=CHCHO$	Kim; Shim, 2004
(**116**) 3-Hexen-1-ol	$CH_3CH_2CH=CH(CH_2)_2OH$	Kim; Shim, 2004
(**117**) 2-Hexenal	$CH_3(CH_2)_2CH=CHCHO$	Kim; Shim, 2004
(**118**) *n*-Hexanal	$CH_3(CH_2)_4CHO$	Kim; Shim, 2004
(**119**) Myriston	$(C_{13}H_{27})_2CO$	Ulubelen; Goren, 1973
(**120**) *n* -Nonacosan	$CH_3(CH_2)_{27}CH_3$	Ulubelen; Goren, 1973
(**121**) *n* -Octacosan	$CH_3(CH_2)_{26}CH_3$	Ulubelen; Goren, 1973
(**122**) Triacontanol	$CH_3(CH_2)_{29}OH$	Ulubelen; Goren, 1973
(**123**) Ginnon	$(C_{14}H_{29})_2CO$	Ulubelen; Goren, 1973

		Ref.
(**124**) Stearic acid	$CH_3(CH_2)_{16}COOH$	Breuer et al., 1987
(**125**) Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	Breuer et al., 1987
(**126**) Linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	Breuer et al., 1987
(**127**) Palmitic acid	$CH_3(CH_2)_{14}COOH$	Ulubelen et al., 1976
(**128**) Lauric acid	$CH_3(CH_2)_{10}COOH$	Ulubelen et al., 1976
(**129**) Arachidic acid	$CH_3(CH_2)_{18}COOH$	Ulubelen et al., 1976
(**130**) Linolenic acid	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	Ulubelen et al., 1976

Figure 5. Varius from *Styrax* species