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THE PHYTOCHEMISTRY OF *ROSA RUGOSA*

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Key Word Index—*Rosa rugosa*; Rosaceae; secondary metabolites; phenolics; terpenoids; tannins; 2-phenoxychromones.

Abstract—The phytochemistry of *Rosa rugosa* is reviewed. The structures of the secondary metabolites identified are listed and aspects of their chemistry are discussed. The metabolites are grouped according to structural classes and include hydrolysable tannins (contained in the leaves and petals), catechin derivatives (roots), flavonoids (leaves), 2-phenoxychromones (leaves), monoterpenes (floral parts, leaves), sesquiterpenes (leaves, especially from glandular trichomes) and triterpenes (leaves and roots). The physiological significance of these metabolites is considered from the perspective of assessing their contribution to the survival and adaptability of the species.

INTRODUCTION

Rugosa rose (*Rosa rugosa* Thunb.) and its horticultural variety (Mei Gui, *R. rugosa* var. *plena*) are known as fragrant and medicinal plants in East Asia. In northern Japan, where this wild rose occurs naturally, the dried petals have been used as antidiarrhoeal and haemostatic agents [1]. In China, dried petals of *R. rugosa* var. *plena* were used in the preparation of rose tea because of their sweet fragrance; the tea was believed to provide nourishment.

In the middle of the nineteenth century, *R. rugosa* was introduced into Europe and North America. Because this wild rose is winter-hardy and is immune to black spot and most other diseases that affect European garden roses, it was attractive to many gardeners [2, 3]. *R. rugosa* was then spread by transplantation for grafting or cross-breeding with European garden roses. It is now not uncommon to see transplanted or naturalized *R. rugosa* and its hybrids in public parks and along the roadside in European and North American cities.

R. rugosa has been found to accumulate heavy metals (e.g. Fe, Cu and Zn) in the leaves. Because these metals can be contributed by air pollutants, it has been suggested that this plant could be useful as an environmental monitor of air and soil pollution [4]. Bagatto *et al.* [5] also have found that such mineral elements accumulate in the leaves, particularly those associated with cynipid galls, and that high levels result in modification of phloem tissues. Several groups have systematically investigated the chemical components in the flowers, fruits, leaves, roots and galls of this plant. The role of the major secondary metabolites in determining the survival and environmental adaptability of *R. rugosa* is of particular interest.

In this review, the metabolites produced by *R. rugosa* are presented according to structural classes. Because more recent investigations have focused mainly on the sesquiterpene metabolites, particularly those produced in the glandular trichomes, more emphasis is given to this section which also includes some results that have not previously been published. Aspects of the chemistry of the secondary metabolites of *R. rugosa* are introduced and the potential physiological significance and role of these metabolites are discussed.

AROMATIC AND PHENOLIC COMPOUNDS

Both aerial and underground parts of *R. rugosa* contain high amounts of phenolic constituents. The petals are rich in hydrolysable tannins, whereas the roots contain abundant amounts of condensed tannins and catechin derivatives. This plant also produces 2-phenoxychromones in the exudate from the glandular trichomes of the leaves.

Hydrolysable tannins

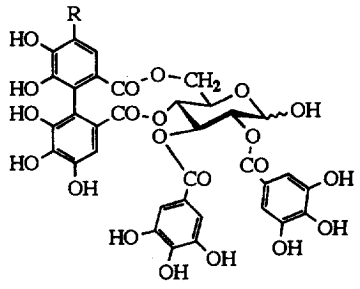
A series of mono- and oligomeric hydrolyzable tannins (**1**–**13**), of high M_r (FW *ca* 1000–2800) have been isolated from fresh petals [6–9]. Tellimagrandin I and II (**1** and **3**) and rugosin A, B and C (**2**, **4** and **6**) are the basic units of the oligomeric tannins, rugosin D, E, F (**10**–**12**; dimeric) and G (**13**; trimeric) [6, 7]. The

ellagitannins tellimagrandin I (**1**) and pedunculagin (**9**) show inhibitory activity towards reverse transcriptase of the retroviruses HIV and HTLV-I [10]. Dried flowers of *R. rugosa* have been used as antidiarrhoeal and haemostatic agents and it is probable that these hydrolysable tannins are the chemical factors involved in the medicinal activity.

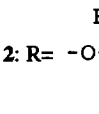
Two simple gallotannins, 1,2,3-trigalloyl-β-D-glucose and 1,2,6-trigalloyl-β-D-glucose, are also found in the petals [6], while cynipid galls are known to accumulate a large amount of phenolics, including gallic acid and gallotannin-like substances. Although a large amount of methyl gallate (**14**) is present in the methanolic extract of the leaves, it can be considered to arise from methanolysis of the gallotannins since **14** could not be detected in the aqueous extracts of the homogenized leaves [11].

Condensed tannins and catechin derivatives

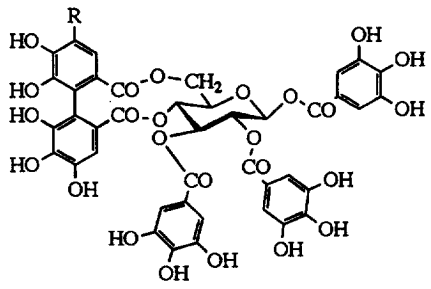
Catechins and other phenolics occur in the immature fruit hips [12], but condensed tannins and catechin derivatives are more abundant in the underground parts of *R. rugosa*. Woody tissues of suckers and anchor roots of a pale red colour contain large amounts of condensed tannins and their oxidized derivatives. After removal of



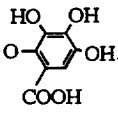
1: R=OH, **tellimagrandin I**



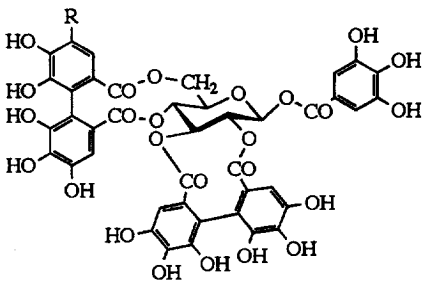
2: R= -O- OH, **rugosin B**



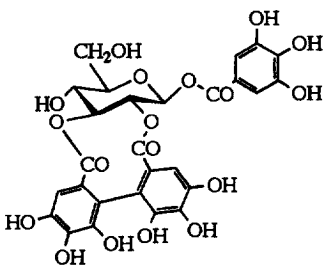
3: R=OH, **tellimagrandin II**



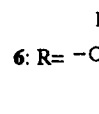
4: R= -O- OH, **rugosin A**



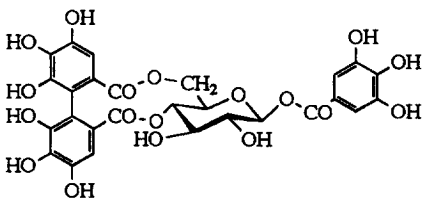
5: R=OH, **casuarictin**



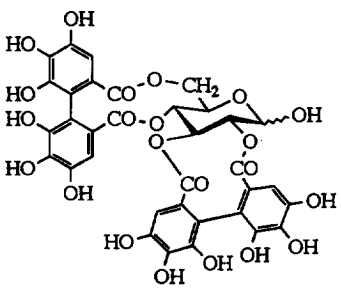
7: **isostrictinin**



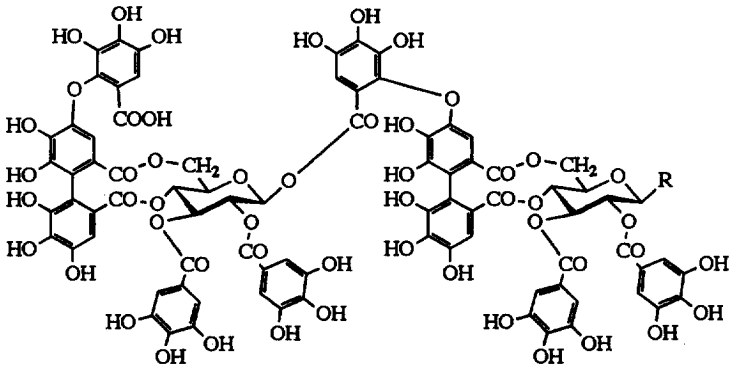
6: R= -O- OH, **rugosin C**



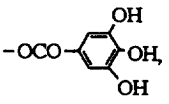
8: **strictinin**

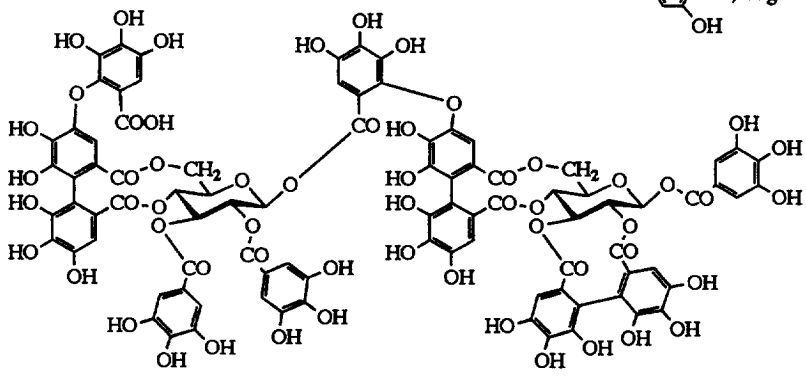


9: **pedunculagin**

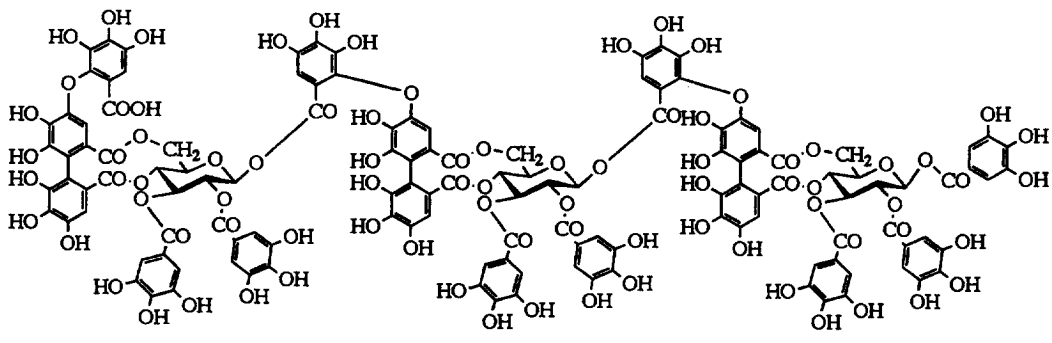


10: R=anomeric OH, rugosin E

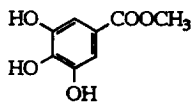
11:R=  rugosin D



12: rugosin F



13: rugosin G



14: methyl gallate

sterols and other lipids by defatting, mixtures of condensed tannins amounted to 10–20% of the fresh weight of tissue.

The major phenolic compounds of low molecular weight are (+)-catechin (**15**) [13], afzelechin-(4$\alpha \rightarrow$8)-catechin (**16**) and procyanidin B-3 (**17**). The polar phenolic fraction also contains several minor catechins and large amounts of catechin oligomers and

polymers. An unidentified phenolic compound containing iron was detected in the mixture and this complex was considered to be a catechin derivative because the catechol group of compound **15** is a typical siderophile. As catechol groups are able to complex with metal cations, it appears that high concentrations of condensed tannins in the underground parts serve to facilitate the uptake of minerals from the nutrient-poor sandy soils. In the Akita prefecture in Japan, the underground parts of *R. rugosa* have traditionally been used as a natural dye for silk, which is known as Akita Hachijo. The condensed tannins play a major role in this staining process.

Flavonoids and 2-phenoxychromones

Immature fruits of *R. rugosa* contain high amounts of kaempferol (**18**), kaempferol 3-*O*-β-glucoside (**19**), quercetin (**20**) and quercetin 3-*O*-β-glucoside (isoquercitrin, **21**) [14], while rutin (quercetin 3-*O*-β-rutinoside, **22**) is the major flavonoid in the roots [15]. These flavonols and their glycosides have been detected in the leaves [16] and compounds **18** and **21** have been isolated from the methanolic extracts of the aerial parts of *R. rugosa* [11]. The simple flavonoids, apigenin (**23**) and 7-*O*-methylkaempferol were isolated as minor components [17]. A kaempferol monoglycoside *p*-coumaroyl ester and related compounds were detected in the leaves but their structures have not yet been elucidated.

2-Phenoxychromones are structurally related to the flavonoids but differ in having an oxygen between rings B and C. Two such compounds, 6-demethoxy-4′-*O*-methylcapillarisin (**24**) and 6-demethoxycapillarisin (**25**), have been isolated from the leaves of *R. rugosa* [17]. This class of compound is of limited distribution; examples have been found in the Leguminosae [18], Berberidaceae [19] and the Compositae [20–22]. The isolation of compound **24** from the leaves of *R. woodsii* [23] suggests that 2-phenoxychromones may occur more generally in *Rosa* species. Although a biogenetic derivation of this class from flavones has been proposed [24], no experimental evidence is available.

Phenylpropanoid derivatives

Eugenol (**26**) and 4-methyleugenol (**27**) were identified as principal odourants of floral fragrance [25–30]. These compounds are abundant in the pollen [29] and compound **27** has been shown to be an attractant to the bumblebee, a known pollinator of *R. rugosa* [31]. β-Phenylethyl alcohol (**28**) is dispersed mainly from the petals [30]. From the odour and content of **28** in the essential oil of *R. rugosa*, it is regarded as a major contributor to the floral fragrance [26, 28].

The 4′-hydroxy-*Z*-cinnamic acid alkyl esters (**29–31**) and 4′-hydroxy-2,3-dihydrocinnamic acid pentacosyl ester (**32**) were found in the ether extract of the leaves [32]. All the cinnamoyl esters possess the *Z*-configuration, which is readily interchanged with the *E*-form by irradiation with sunlight. It is suggested that these compounds are components of the membrane of the cells or chloroplasts. Because in such an environment the phenylpropanoid moiety is most likely situated on the outer surface of the membrane, and given an UV absorption maximum of 370 nm for the *Z*-isomer, it is tempting to suggest that they might function as light sensors or UV protectors of the biomembranes.

Benzyl alcohol was also identified as a component of the volatile fraction [30]. Significant amounts of pyrocatechol and pyrogallol are produced when the mature leaves are physically damaged and soaked in tap water [11]. These phenolics may be produced from more complex phenolics by bacterial processes similar to those in which 4-hydroxycinnamic acids are converted into the corresponding styrenes [33]. No attempts to isolate catechol-releasing bacteria or to identify the original compounds have been made.

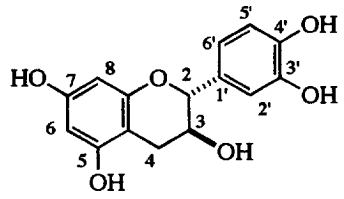
TERPENOIDS

Hemiterpenes and monoterpenes

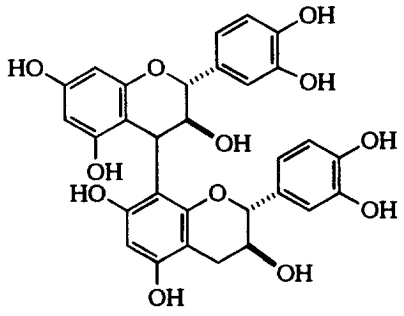
Several volatile terpenoids have been identified as fragrant components of the flowers of *R. rugosa*, its varieties and hybrids. The hemiterpenes, 2-methylbutan-2-ol (**33**) and 3-methylbutan-1-ol (**34**) were detected in trace amounts in the essential oil from the flowers [26] and in the headspace of floral green parts [29], respectively. 6-Methyl-hept-5-en-2-one (**35**) was identified from the pollen [29].

The more abundant monoterpenes in the floral essential oil of *R. rugosa* and *R. rugosa* var. *plena* were citronellol (**36**) and geraniol (**39**) [25, 26, 28–30]. Other volatile monoterpenes detected from *R. rugosa* var. *plena*, and of more than 0.05% relative abundance (by GC), were citronellyl acetate (**37**), citronellyl formate (**38**), nerol (**41**), linalool (**43**), geranial (**44**), neral (**45**), citronellal (**46**), geranylacetone (**47**), α-terpineol (**48**), *cis*-rose oxide (**49**) and *trans*-rose oxide (**50**) [26]. Ohno and Tanaka [25] detected significant amounts of geranyl acetate (**40**) and neryl acetate (**42**). Some monoterpene hydrocarbons, α-pinene (**51**), *E*-β-ocimene (**52**) and limonene (**53**), have been detected in the essential oil of *R. rugosa* [26, 29] and a hybrid [27].

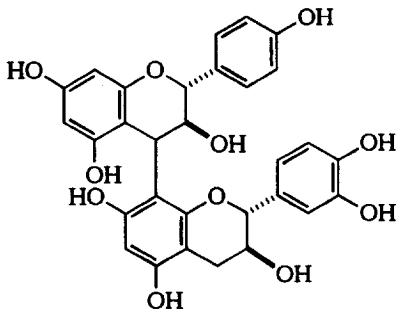
An investigation of the volatile components of each floral part (pollen, anthers, green sepals and petals) by a headspace absorption–desorption technique has revealed that the content and composition of monoterpenes in each part are clearly different [29, 30]. The monoterpene alcohols, **36**, **39** and **41**, were mainly dispersed from the flower petals, whereas the pollen and anthers were rich in their corresponding acetates, **37**, **40** and **42**. Such variations between the floral parts suggest a different role of each part in pollinating events [30].



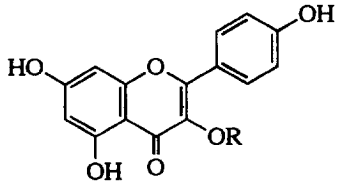
15: (+)-catechin



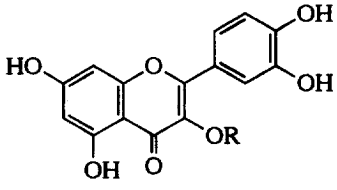
17:procyanidin B-3



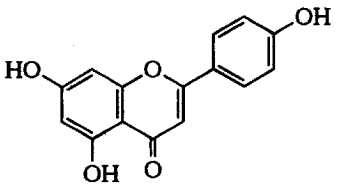
16: afzelechin-(4α->8)-catechin



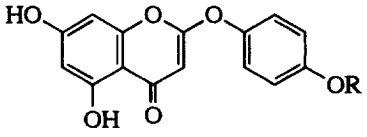
18: R=H, kaempferol
19: R=β-glucose



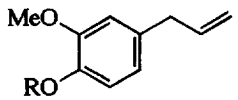
20: R=H, quercetin
21: R=β-glucose, isoquercitrin
22: R=β-rutinose, rutin



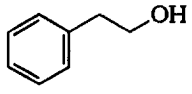
23: apigenin



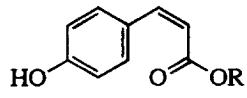
24: R=CH_3, 6-demethoxy-4'-O-methylcapillarisin
25: R=H, 6-demethoxycapillarisin



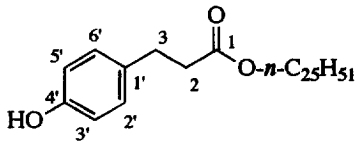
26: R=H, eugenol
27: R=CH_3, methyleugenol



28:β-phenylethyl alcohol



29: R=*n*-$C_{22}H_{45}$
30: R=*n*-$C_{26}H_{51}$
31: R=*n*-$C_{28}H_{53}$



32: pentacosyl-2,3-dihydro-4'-hydroxycinnamate

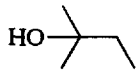
From the dichloromethane-soluble extract of young leaves of *R. rugosa*, **41** (major) and **43** (minor, but a substantial odourant) were identified. Both compounds contribute to the sweet green-like note of the leaves [34]. Several unidentified monoterpenes, together with some sesquiterpene alcohols and C_6-volatile compounds, were detected in the fraction containing the leaf fragrance and, probably, also contribute to it [34].

The methanolic extracts of the floral parts contain monoterpene glucosides and it has been suggested that some of the monoterpenes are stored in this way in the tissues and released by the action of a β-glucosidase [35].

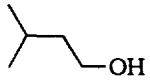
Sesquiterpenes

Several sesquiterpenes representing the bisabolane, acorane and carotane classes have been isolated and characterized from *R. rugosa*. Only a few species of the Rosaceae are known to produce sesquiterpenes and all of them belong to the genus *Rosa*. *R. rugosa*, its varieties (e.g. *R. rugosa* var. *plena*) and hybrids (e.g. 'Kohamanasu', a natural hybrid between *R. rugosa* and *R. multiflora*, or 'Hansa', a horticultural hybrid of *rugosa* [2]) are, to date, the only species known to produce carotane sesquiterpenes.

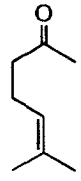
The unique metabolic characteristics of the *R. rugosa* group are based on the presence of glandular trichomes



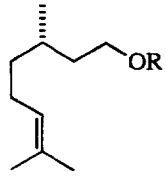
33: 2-methylbutan-2-ol



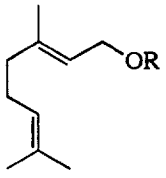
34: 3-methylbutan-1-ol



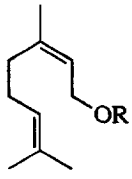
35: 6-methylhept-5-en-2-one



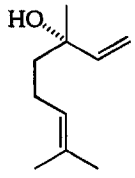
36: R=H, citronellol
37: R=Ac, citronellyl acetate
38: R=CHO, citronellyl formate



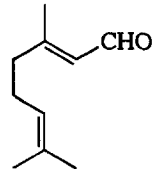
39: R=H, geraniol
40: R=Ac, geranyl acetate



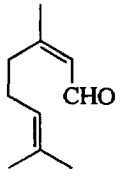
41: R=H, nerol
42: R=Ac, neryl acetate



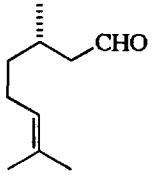
43: linalool



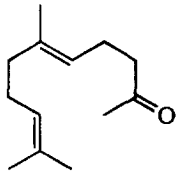
44: geranial



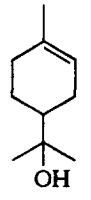
45: neral



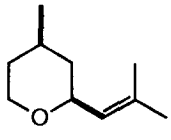
46: citronellal



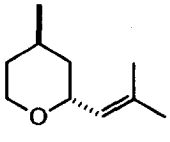
47: geranyl acetone



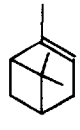
48: α-terpineol



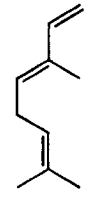
49: *cis* -rose oxide



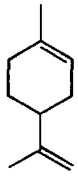
50: *trans* -rose oxide



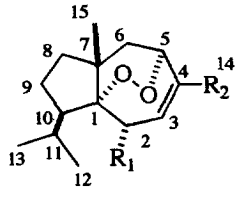
51: α-pinene



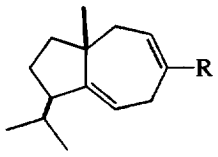
52: *trans*-β-ocimene



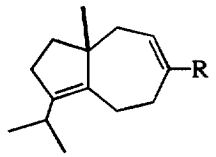
53: limonene



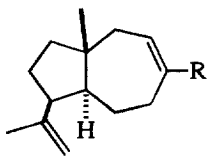
54: R_1=OH, R_2=CHO, rugosal A
55: R_1=OH, R_2=COOH, rugosic acid A
56: R_1=OH, R_2=COOMe, rugosic acid A methyl ester
57: R_1=OH, R_2=CH_3, 1,5-epidioxy-2-hydroxycarot-3-ene
58: R_1=OOH, R_2=CHO, 1,5-epidioxy-2-hydroperoxycarot-3-en-14-al
59: R_1=OOH, R_2=COOH, 1,5-epidioxy-2-hydroperoxycarot-3-en-14-oic acid



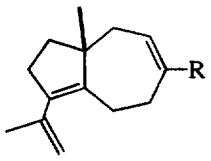
60: R=CHO carota-1,4-dienaldehyde
61: R=COOH carota-1,4-dienoic acid
62: R=CH_3 carota-1,4-diene
63: R=CH_2OH carota-1,4-dienol



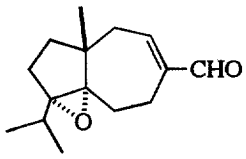
64: R=CHO daucenal
65: R=CH_3 daucene



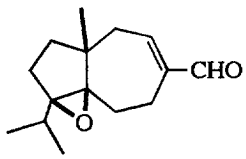
66: R=CHO isodaucenal
67: R=COOH isodaucenoic acid
68: R=CH_3 isodaucene
69: R=CH_2OH isodaucenol



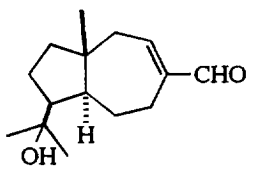
70: R=CHO 11,12-dehydrodaucenal
71: R=COOH 11,12-dehydrodaucenoic acid



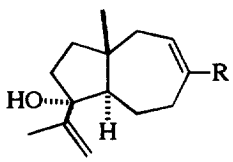
72: epoxydaucenal A



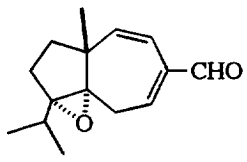
73: epoxydaucenal B



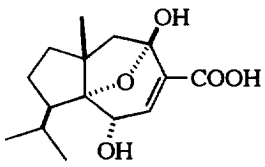
74: 11-hydroxy-12-hydroisodaucenal



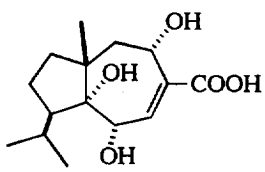
75: R=CHO 10-hydroxyisodaucenal
76: R=CH_3 10-hydroxyisodaucene



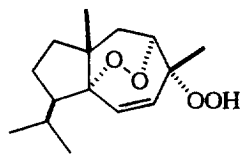
77: rosacarotanal



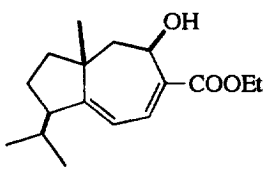
78: rugosic acid B



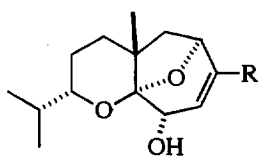
79: rugosic acid C



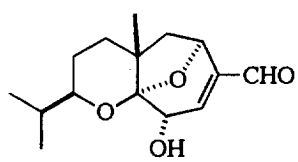
80: 1,5-epidioxy-4-hydroperoxycarot-2-ene



81: 5-hydroxycarota-1,3-dienoic acid ethyl ester (artifact?)



82: R=CHO rugosal D
83: R=COOH rugosic acid D



84: epirugosal D

which are densely distributed, along with leaf veins, on the undersurface of the leaflets and actively exude syrup-like droplets from the tips (*ca* 10–15 g kg^{-1} fresh leaves). The exudate is mainly composed of sesquiterpenes [30, 36], 60–70% of which consists of sesquiterpene acids. An efficient technique for the separation of the glandular trichomes of *R. rugosa* has been developed and this should facilitate biosynthetic studies on the sesquiterpenes produced in the trichomes [37].

Carotanes (daucanes)

Twenty-eight carotane sesquiterpenes (**54–81**), most of which are new, have been isolated from *R. rugosa*

[34, 36, 38–44]. These include rugosal A (**54**) and rugosic acid A (**55**) whose structures were first reported in 1989 [38]. The three known carotane hydrocarbons, carota-1,4-diene (**62**), daucene (**65**) and isodaucene (**68**) [42, 45–47] have also been isolated.

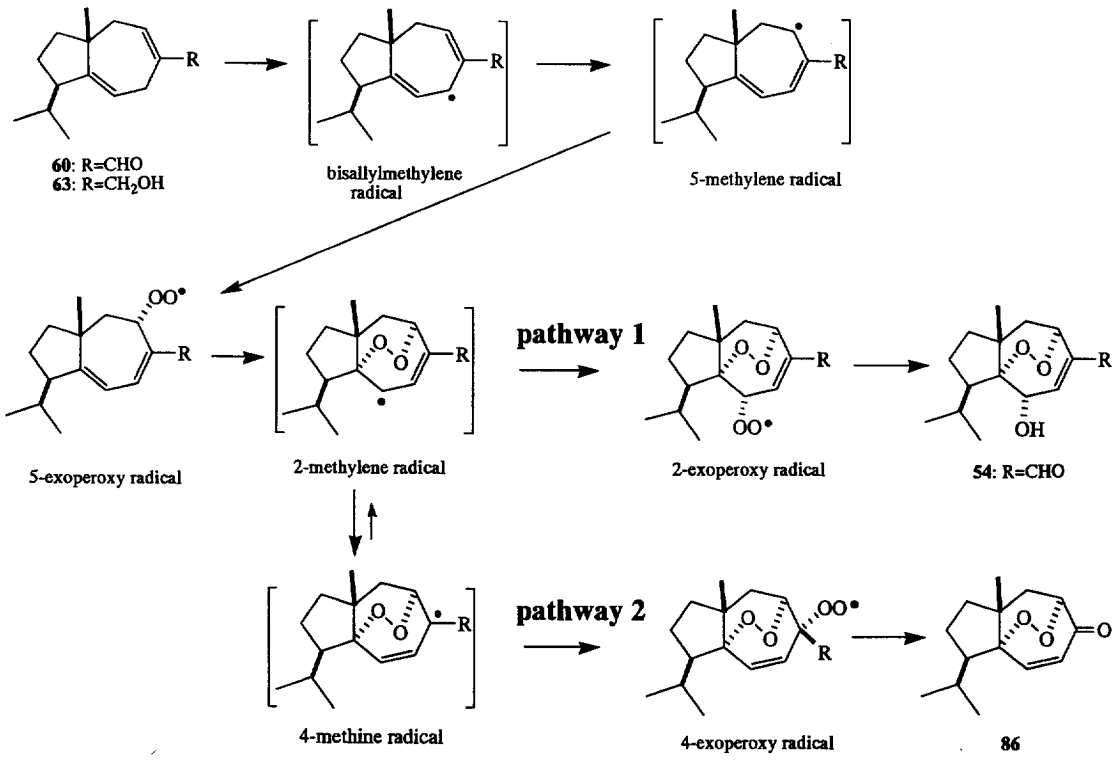
Rugosal A (**54**) was first obtained from damaged *R. rugosa* leaves as an antifungal substance (minimum inhibitory concentration towards *Pyricularia oryzae*: 6.3 ppm). Its structure was elucidated by means of chemical characterization and spectroscopic analysis, including Inadequate NMR techniques. Rugosal A was shown to contain the bicyclic carotane skeleton which included an 1,5-epidioxy bridge and an allylic hydroxyl which was hydrogen-bonded to one of the epidioxy oxygens [38]. The relative configuration was determined from NOESY measurements [38] and the absolute configuration was established by application of the exciton-chirality method to a 2-benzoate derivative [48].

A likely precursor of **54**, carotan-1,4-dien-14-al (**60**), was also isolated from the less polar fractions of the extract [39]. In chemical studies, the diene aldehyde (**60**) and other 1,4-diene derivatives prepared synthetically, were oxidized to yield 1,5-epidioxy-2-hydroperoxycarot-3-enes and 1,5-epidioxy-14-norcarot-2-en-4-one (**86**) with identical stereochemistry to that of the natural products. The intermediate species, 5-hydroperoxy-1,3-dienes and 2-hydroperoxy-1,5-epidioxycarot-3-enes, were also identified, providing evidence for the radical nature of the peroxidation process (Scheme 1) [49, 50]. A competing set of reactions leads to the formation of the norcarotane derivative (**86**) (Scheme 1; pathway 2) [50].

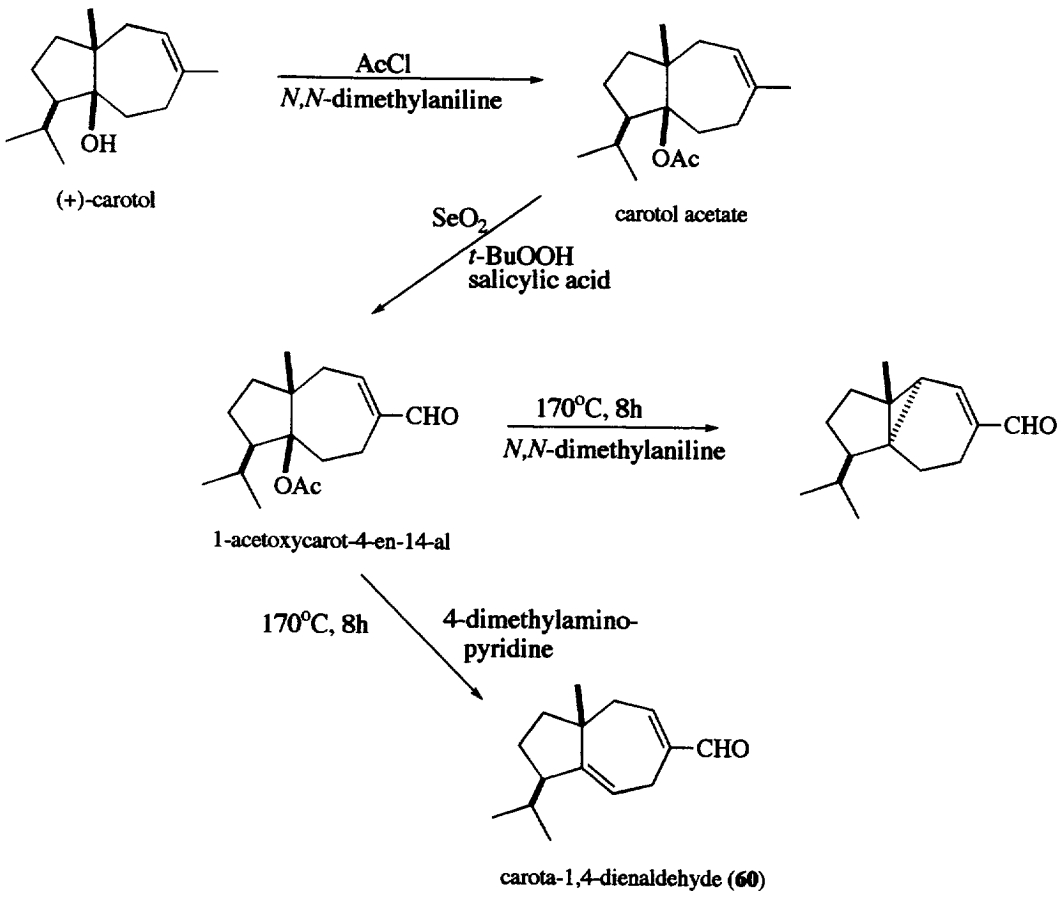
Synthesis of carota-1,4-dien-14-al (**60**) from (+)-carotol, readily available from the oil of carrot seeds, has been achieved (Scheme 2) [51], thus providing an alternative source of this compound. Because a total synthesis of (+)-carotol has been described [52], and since compound **60** has been converted into rugosal A (**54**) in high yields, this constitutes a formal total synthesis of rugosal A. As shown in Scheme 2, attempts to achieve elimination of acetic acid from 1-acetoxycarot-4-en-14-al led to the formation of a compound that contained a cyclopropane ring arising from bond formation between C-1 and C-6. The significance of this is a possible biosynthetic intermediate lining the carotane and the acorane sesquiterpenes is discussed below.

Levels of the three major carotane sesquiterpenes (**54**, **55** and **60**) in *R. rugosa* showed significant seasonal variations [53]. Compound **60** was detected during the budding and flowering stages coinciding with maximum production of 1,5-epidioxides ($>500\ mg\ kg^{-1}$ of leaves), but its production in the leaves stopped during the ripening and leaf senescence stages. This study revealed that autoxidation of compound **60** occurred in the exudate [36, 53].

A characteristic feature of the carotanes produced by *R. rugosa* is the presence of oxygenation at C-14, a feature rarely encountered in the carotanes from other sources such as the Umbelliferae, Compositae, lower plants and microorganisms [54]. Only four examples of



Scheme 1. Autoxidation of carota-1,4-diene derivatives to 1,5-epidioxy compounds.



Scheme 2. Conversion of (+)-carotol to (−)-carota-1,4-dienaldehyde.

C-14 oxygenated carotanes have been reported from these sources [55–58], including **54**, which was isolated from the roots of *Nardostachys chinensis* (Valerianaceae) [58], and aspterric acid, isolated from *Aspergillus terreus* [57]. Oxygenation at C-14 appears to be a characteristic of *R. rugosa* and this is the main reason why most carotanes from this plant are new compounds. Some carotane-derived sesquiterpenes have also been isolated from *R. rugosa*. The structures of four secocarotanes (**82–85**) [40, 43], which lack the C1-C10 bond, and a 14-norcarotane (**86**) [36] have been elucidated.

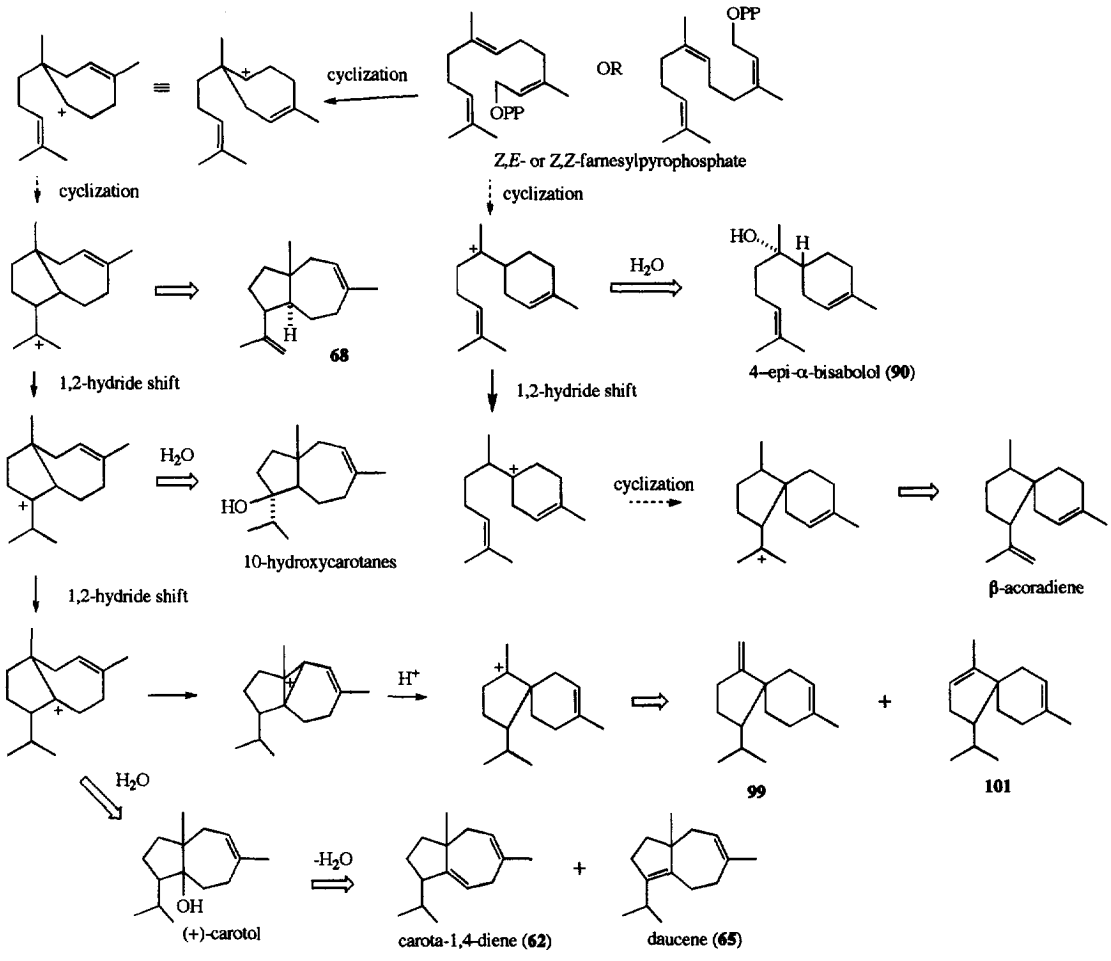
Bisabolanes

All the bisabolane sesquiterpenes (**87–97**) isolated from *R. rugosa* to date [43, 44, 59, 60] are of the α-bisabolol type, containing oxygenation at C-8. This feature is common to many other bisabolanes from the Compositae and other plant sources and probably reflects the neutralization of a carbocation at C-8 following biosynthetic cyclization of farnesyl pyrophosphate [61]. This hydroxylation is equivalent to that which occurs to generate the tertiary hydroxyl group in (+)-carotol (Scheme 3) [62].

Another characteristic feature of the bisabolanes from *R. rugosa* is oxygenation of the pendant allylic carbon at C-7. Similarly oxygenated bisabolanes have been isolated from pine [63, 64] and fungal sources [65] and examples of C-7, C-8-dioxygenated bisabolanes have been isolated from the Compositae [66–70].

Interestingly, some other wild roses (e.g. *R. woodsii* and *R. acicularis* distributed throughout inland), closely related to *R. rugosa* but lacking glandular trichomes, have been found to produce similar bisabolanes but the presence of carotane sesquiterpenes in these related varieties has not yet been confirmed [23]. Whereas *R. rugosa* produces relatively higher amounts of bisabolanes with a carboxylic acid or a methoxycarbonyl at C-7, hamanasic acid (**89**) and bisaborosaol A (**90**) respectively, *R. woodsii* and *R. acicularis* accumulate amounts of the corresponding derivatives with a C-7 hydroxymethyl (hamanasol A) and aldehyde groups (hamanasal A, **88**). In *R. rugosa*, no hamanasol A has been detected and compound **88** is present in small amounts. This observation suggests that monooxygenase activity is present in both species and that secondary oxidation is more important in *R. rugosa*.

The most characteristic feature of the bisabolane sesquiterpenes from *R. rugosa* is the stereochemistry of the asymmetric carbon at position 4. In 8-hydroxy-



Scheme 3. Biogenetic relationships between carotane (daucane), epibisabolane and acorane sesquiterpenes. Large arrows (⇒) show steps that yield stable products from unstable cationic intermediates, while (→) and (- - →) show new C–C bond formation and cation isomerization, respectively.

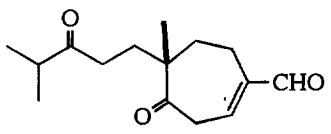
bisabolane derivatives, the C-4 asymmetric carbon makes the major contribution to the optical rotation values of these compounds, whilst the C-8 carbon contributes less than ±2° to the specific rotation [68, 71, 72]. All the major bisabolanes from *R. rugosa* show simple positive ORD curves, indicating the 4*R*-configuration [44, 59, 60]. Some 8-hydroxybisabolane derivatives from the Compositae, whose stereochemistry has been obtained by synthesis and/or chemical correlation to be 4*S*,8*S*, have negative specific rotation in agreement with their 4*S*-absolute configuration [68, 72].

From the exudate of the glandular trichomes of *R. rugosa* a small amount of (+)-4-epi-α-bisabolol (**87**) was isolated and characterized spectroscopically [44]. Direct comparison with (−)-α-bisabolol showed the two to be diastereoisomers. Thus, the 8-hydroxybisabolanes from *R. rugosa* have the 4*R*,8*S* absolute configuration. Although some examples of plants producing **87** or (−)-4-epi-α-bisabolol (4*S*,8*R*) are known [72–77], bisabolanes with the 4*R* configuration are relatively rare.

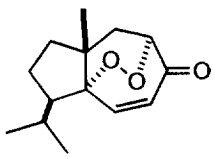
Most of the carotane acids in the exudate are derived from the corresponding aldehydes, while the bisabolane acids are exuded as sodium salts. From the amount of acids produced, it can be calculated that 1 kg of leaves exude about 400 mg of Na^+ from the glandular trichomes. Because *R. rugosa* is salt-tolerant [78], it is possible that the sesquiterpene acids might function as carriers of sodium cations to assist in the excretion of excess sodium. The fact that the major bisabolane sesquiterpenes of *R. woodsii* and *R. acicularis* are of the aldehyde type (**88**) may support this hypothesis. The norbisabolane (**97**) isolated from *R. rugosa* probably arises from enymic decarboxylation of hamanasic acid A (**89**) [44].

Acoranes and other classes

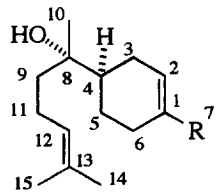
The acorane sesquiterpenes (**98–101**) isolated from *R. rugosa* [41–43], unlike the carotanes and bisabolanes, do not contain oxygenation of the pendant carbon arising from C-13 of farnesyl pyrophosphate. In



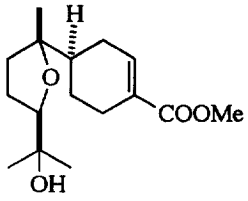
85: secocarotanal



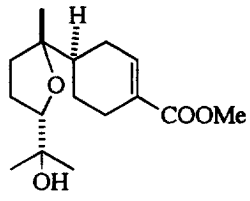
86: 1.5-epidioxy-14-norcarot-2-en-4-one



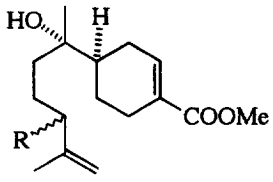
87: R=CH_3, (+)-4-epi-α-bisabolol
88: R=CHO, hamanasal A
89: R=COOH, hamanasic acid A
90: R=COOMe, bisaborosaol A



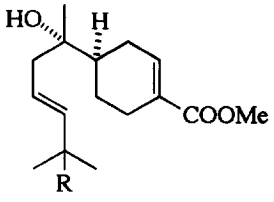
91: bisaborosaol B1



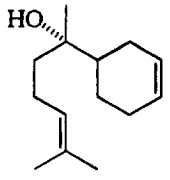
92: bisaborosaol B2



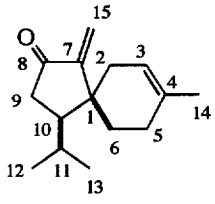
93: R=OOH bisaborosaol C1/2
94: R=OH bisaborosaol E1/2



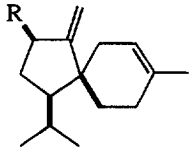
95: R=OOH bisaborosaols D
96: R=OH bisaborosaol F



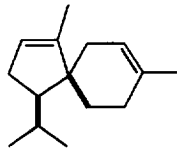
97: 7-nor-α-bisabolol



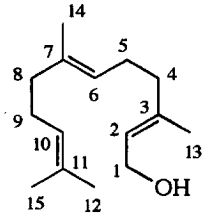
98: rosacorenone



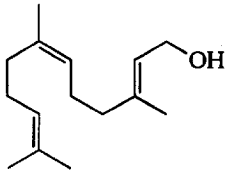
99: R=H acora-3(4),7(15)-diene
100: R=OH rosacorenol



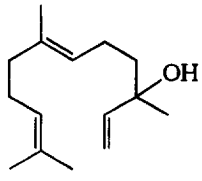
101: acoradiene III



102: *E,E*-farnesol



103: *E,Z*-farnesol



104: nerolidol

fact, acorane sesquiterpenes were the major constituents of the hydrocarbon fraction [42]. The co-occurrence of carotane and acorane sesquiterpenes in *R. rugosa* suggests a biosynthetic relationship between the two classes, particularly when chemical interconversion between them is taken into account [79, 80].

Because the acoranes of *R. rugosa* do not appear to be derived simply from an acorane C11-carbocation (Scheme 3), it is tempting to speculate that they arise from the carotane C1-carbocation. The two acoranes (**99**, **101**), containing a double bond at C7-C15 and C7-C8 respectively, support this speculation because they appear to arise from a C7-carbocation. Moreover, carotol has been chemically converted to dienes **99** and **101** [80].

From the essential oils of the flowers of *R. rugosa* var. *plena*, *E*, *E*-, *E*, *Z*-farnesol (**102**, **103**) and nerolidol (**104**) were detected by GC analysis (2.42, 1.75 and

0.25%, respectively) [26]. α-Farnesene was identified from the pollen [30].

Triterpenoids, steroids, tocopherol and carotenes

A mixture of sitosterol and campesterol 3-*O*-β-glucosides (**105, 106**) were obtained from the roots of this plant [81]. The 28-*O*-β-glucosides of eucaphic, tormentic and arjunic acids (**107–109**) were isolated following screening of the root components for hypolipemic activity [82]. Some sterols, including sitosterol, from the aerial parts were identified in a study on the disease resistance of the roses [83]. The steroid content of *R. rugosa* and other resistant types was realtively low, whereas roses susceptible to fungal infections had higher concentrations of sterols in the leaves.

Tocopherols and carotenes, both of which function as antioxidants in the thylakoid membranes, are abundant in the leaves and fruits. Because of the high amounts of β-carotene and γ-tocopherol (Vitamin E), *R. rugosa* is regarded as a good vitamin source [84]. In the fruits, the levels of β-carotene and lycopene are particularly high, whereas xanthophylls are present as minor comonents [85]. A positive correlation was observed between the amount of carotenes and the altitude at which the plant was grown [86]. From an investigation of the carotenes in the leaves, it was found that levels of xanthophyll epoxides increased at the senescence stage [87]. The seed oil of *R. rugosa* is rich in γ-tocopherol [88].

FATTY ACID DERIVATIVES

GC–mass spectral analysis of the volatiles from the flowers revealed the presence of pentanol (**110**), hexanol (**111**), hexyl acetate (**112**) and *Z*-3-hexenyl acetate (**116**) [26]. Several long-chain alkanes were identified from the headspace of pollen and pollen-concrete extracted with pentane [29]. Alkyl-2-ones in the series C7, C9, C11, C13 and C15 (**117–121**), the tetradecyl and hexadecyl acetates (**113** and **114**), tetradecanal (**124**) and hexadecanal (**125**) were also characterized. Compounds **113, 120** and **124** were the major components in the pollen [30].

In addition to the aliphatic compounds above, the essential oil of *R. rugosa* var. *plena* also contained heptanal (**123**) and heptan-2-ol (**126**) and traces of *Z*-3-hexenol (**115**) [26]. Extraction of young leaves with dichloromethane gave an extract which contained hexanal (**122**) and *Z*-3-hexenyl acetate (**116**) but no *Z*-3-hexenol (**115**) which, however, was detectable in damaged leaves of *R. rugosa*.

SUGARS AND OTHER POLAR COMPOUNDS

The fruit (hips) and achenes of *R. rugosa* are rich in ascorbic acid [84, 89, 90]. This compound and an unidentified water-soluble compound function as germination inhibitors of the plant [91]. Other carbohydrates present in the hips include xylose, fructose, glucose and sucrose [92]. Carbohydrate-like substances are also present in the exudate from glandular trichomes but these have not received much attention. No alkaloids appear to be produced by *R. rugosa* or other members of the Rosaceae.

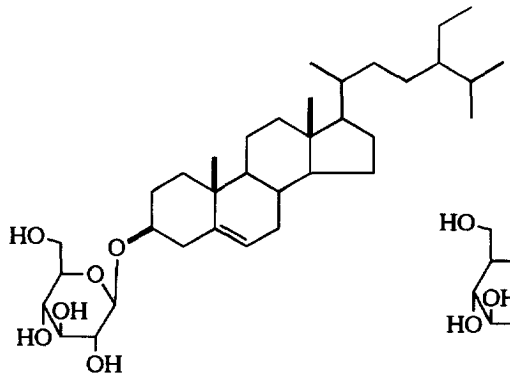
CONCLUSION

In its natural habitat, *R. rugosa* is distributed throughout the sandy soil of coastal areas and grows in an environment where conditions can be harsh; exposure to strong UV light in summer and extreme cold (−20°) in winter [3]. In addition, the physical and chemical properties of coastal sandy soils are limiting. The soil is poor in essential trace elements, phosphate and nitrogen sources, while in excess of sodium chloride carried from the sea water continually challenges the plant [3].

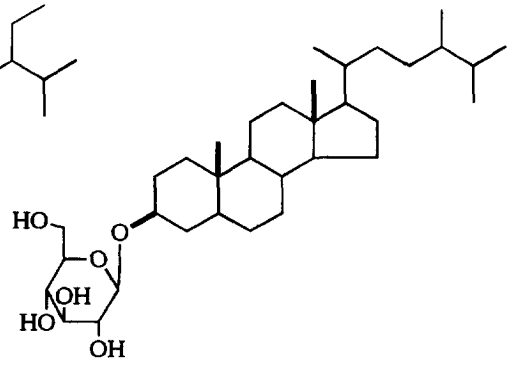
Secondary metabolites of plants are known to function as chemical messengers or as antipest agents [3, 93]. In the case of *R. rugosa*, the roles of the secondary metabolites would appear to be greater than just to confer protection against pathogenic microorganisms and insect herbivores, whose populations in coastal areas are low. In urban areas, aphids and cynipids prefer *R. rugosa* to other wild or garden roses [3], but these parasites are seldom observed on the plant in its natural habitat. Because the amount and composition of secondary metabolites in wild and transplanted plants do not appear to vary greatly, the difference in parasite infestation reflects differences in their populations.

What then is the basic role of the secondary metabolites in *R. rugosa*? After considering the different structural types associated with different tissues, it would appear that they reflect the adaptability of this plant to the environment. Many secondary metabolites probably play key roles in the survival of the plant: nutrient uptake (condensed tannins and other phenolics), protection from UV light (antioxidants and phenolics), excretion of sodium chloride (sesquiterpene acids) and reproduction by effective pollination (monoterpenes and other volatile compounds). *R. rugosa* is thus able to survive in harsh conditions where there is less competition and less pressure from parasites—conditions found in the coastal zones and in artificial gardens. It is interesting to note that *R. rugosa* has become naturalized on the eastern coast of New England [2], whereas the wild colonies in Hokkaido are being driven out by naturalized meadow grasses.

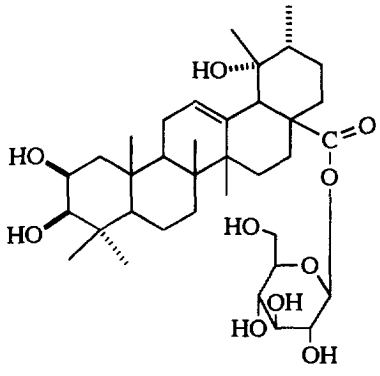
It is possible that the secondary metabolites of *R. rugosa* first developed to enhance the adaptability to the coastal environment and, fortuitously, some of these provided resistance against the diseases of the garden roses. Chemical adaptability in a plant, as expressed by the type and quantity of its secondary metabolites, appears to be dynamic and flexible and, as with



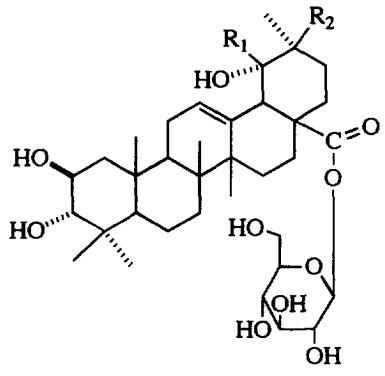
105: sitosterol 3-O-β-glucoside



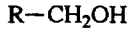
106: campesterol 3-O-β-glucoside



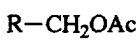
107: R_1=H, R_2=CH_3, euscaphic acid 28-β-glucoside



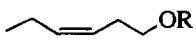
108: R_1=CH_3, R_2=H, tormentic acid 28-β-glucoside
109: R_1=H, R_2=CH_3, arjunic acid 28-β-glucoside



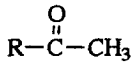
110: R=C_4H_9, pentanol
111: R=C_5H_{11}, hexanol



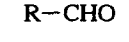
112: R=C_5H_{11}, hexyl acetate
113: R=$C_{13}H_{27}$, tetradecyl acetate
114: R=$C_{15}H_{31}$, hexadecyl acetate



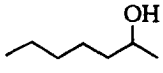
115: R=H, Z-3-hexenol
116: R=Ac, Z-3-hexenyl acetate



117: R=C_5H_{11}, heptan-2-one
118: R=C_7H_{15}, nonan-2-one
119: R=C_9H_{19}, undecan-2-one
120: R=$C_{11}H_{23}$, tridecan-2-one
121: R=$C_{13}H_{27}$, pentadecan-2-one



122: R=C_5H_{11}, hexanal
123: R=C_6H_{13}, heptanal
124: R=$C_{13}H_{27}$, tetradecanal
125: R=$C_{15}H_{31}$, hexadecanal



126: heptan-2-ol

morphological characteristics, reflects adaptability to the environment.

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