Biomed. Papers 149(1), 3–28 (2005)

MYRRH – *COMMIPHORA* CHEMISTRY

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Received: May 25, 2005; Accepted: June 5, 2005

Key words: Myrrh/Commiphora

Myrrh and opopanax has been used throughout history in incense and as a perfume. Since Bible times it has been used for the treatment of wounds. The first attempts to identify content compounds were almost 100 years ago. In this review we discuss the present state of knowledge in the chemistry of substances of *Commiphora* spp.

INTRODUCTION

Myrrh and the similar but lower quality opopanax are the hardened, resinous exudates obtained from trees of certain *Commiphora* species of the *Burseraceae* family. Myrrh and opopanax oils are occasionally used as flavouring agents. Somalia and Ethiopia are by far the largest producers of the two resins. Northern Somalia is the world's largest source of incense and myrrh, which are forestry products. Aromatic flora, producing frankincense and myrrh, are indigenous to the mountain slopes. Somalia supplies most of the world's myrrh and opopanax (about 1 500 tonnes in 1987). The People's Republic of China is the largest market for all two resins, mainly for use in traditional medicines. In early 1994, clean Somali myrrh was available at US $ 5/kg. Somali opopanax was priced at US $ 3.50/kg (clean) and US $ 3.00/kg (natural).

Commiphora species are small trees or shrubs with short, thorny branches. True myrrh is produced by *C. myrrha*, a variable species found in southern Arabia and northeast Africa (chiefly Somalia) as far south as northeast Kenya. Other resin-producing *Commiphora* occur in southern Arabia, Sudan, Ethiopia, Eritrea, Somalia and Kenya. *C. erythraea* and *C. kataf*, the main sources of opopanax, are abundant in many parts of southern Arabia, Somalia, eastern Ethiopia and Kenya.

In Arabic the word *murr* means "bitter", it has been used throughout history in incense and as a perfume. It is said that the Greek soldiers would not go into battle without a poultice of myrrh to put on their wounds. It is often used in toothpastes and in the perfume industry. It tends not to dissolve very well in water however.

Myrrh consists of water-soluble gum, alcohol-soluble resins and volatile oil. The gum contains polysaccharides and proteins, while the volatile oil is composed of steroids, sterols and terpenes. Myrrh's characteristic odor is derived from furanosesquiterpenes.

Since Bible times it has been used as a medicine and wound dressing and has been closely associated with the health and purification rituals of women. It was first described in the Chinese medical literature. The use of myrrh medicinally was recorded in China in A.D. 600 during the Tang Dynasty. Myrrh is used today in Chinese medicine to treat wounds, relieve painful swelling, and to treat menstrual pain due to blood stagnation. Myrrh is called *mo yao* in China. It has long been used in the Ayurvedic system of medicine.

Commiphora opobalsamum balm is the thickened gum from the juice of the balsam tree, which was abundant in Judea. It is native to southern Arabia and Abyssinia, was cultivated on the plains of Jericho and the Jews believed it was planted by King Solomon. According to history the Queen of Sheba brought balm to Solomon on the occasion of her visit. Balm was rare and costly when exhibited in Rome for all people to see. After the conquest of Judah, it was brought by Pompey for display. When Vespasian destroyed Jerusalem, balm was among his spoils. Balm was the emblem of Palestine and newly cultivated shrubs were protected by sentries.

General

On this place we must mention the most known *Commiphoras*, namely *Commiphora myrrha* (Nees) Engl., true myrrh, officinal myrrh, Heera Bol tree; *C. myrrha* (Nees) Engler var *molmol* Engler (*C. molmol* Engl. ex Tschirch), Somalian myrrh; *Commiphora abyssinica* (Berg) Engler (syn. *Commiphora madagascarensis* Jacq.), Arabian myrrh, Abyssinian myrrh; *Commiphora africana* (A. Rich.) Engl., myrrh, African bdelium; *Commiphora guidottii* Chiov., sweet myrrh, habag-hady (name in Somalia);

Commiphora mukul (Hook ex Stocks) Engl. (*Commiphora wightii* (Arnott.) Bhanol.), guggul, guggulu, false myrrh; *Commiphora opobalsamum* (*C. gileadensis* (L.) Christ.; *Balsamodendron meccansis Gled.*), balm of the Mecca; *Commiphora erythraea* (Ehrenb.) Engl., opopanax (originally *Hemprichia erythraea*); *Commiphora erythraea* var. *glabrascens*, opopanax and *Commiphora kataf* (Forssk.) Engl., african opopanax.

Pernet mention the places of known *Commiphoras*[1]: *Commiphora Jacq*. – over 200 species around Read Sea in East Africa, 20 species in Madagascar and 6 in India; *C. abyssinica* Engl., "myrrh" –Ethiopia and Jemen; *C. agallocha* Eng. – India; *C. africana* – Ethiopia and subsaharian Africa

C. aprevali (Baill) Guill. – Madagascar; *C. Boiviniana* Engl. – tropic Africa; *C. charten* Birdw. – tropic Africa; *C. erythraea* Engl., "opopanax" or "bisabol" – mediteranean region and Ethiopia; *C. kataf* Engl., "african opopanax" – Arabia; *C. merkeri* Engl. – tropic Africa; *C. mukul* Engl. – India; *C. myrrha* Engl., "officinal myrrh" – Arabia and Lybia and Somalia; *C. opobalsamum*, "balm of the Mecca" – Arabia and Somalia; *C. Pervilleana* Engl., "matambelona" – Madagascar; *C. pilosa* Engl. – tropic Africa; *C. pyracanthoides* (syn. *C. glandulosa* Schinz.) – tropic Africa; *C. Roxburgii* Alston (syn. *C. agalocha*); *C. Schimperi* Engl. – Ethiopia and Erythrea; *C. simplicifolia* H. Perr., "sangathy" – Madagascar; *C. ugogensis* Engl. –tropical Africa and *C. Zimmermannii* Engl. – tropical Africa.

The following new species were described by Thulin[2]: *Commiphora arenaria* from bushland on sand in south-central Somalia, *C. gardoensis* from limestone slopes in the Qardho area in north-eastern Somalia, *C. stellatopubescens* from bushland on limestone outcrops or stony ground in the Hiiraan Region in south-central Somalia, *C. spinulosa* from limestone rocks on the escarpment along the Gulf of Aden in northeastern Somalia, *C. lobatospathulata* from bushland on sand in central and southcentral Somalia, *C. quercifoliola* from bushland on shallow soil over limestone near Eil in north-eastern Somalia, *C. chiovendana* from bushland in northern and central Somalia, *C. multifoliolata* from limestone hills and ridges in south-western Somalia, *C. murraywatsonii* from limestone outcrops near Hobyo in central Somalia, and *C. kucharii* from bushland on shallow soils over limestone in central and southern Somalia.

The next publication goes further to inform as about present state of distribution of *Commiphora* spp. (ref.[3]) *Commiphora myrrha* is the chief source of myrrh today, but *C. erythraea* was the principal source of ancient and classical time. A number of oleo-gum-resins called bdelliums are produced in Arabia and Somalia from various species of *Commiphora* and resemble myrrh; these were probably counted as myrrh in classical times and are probably used for adulteration today. The "perfumed bdellium" (opopanax or bisabol myrrh) is from *C. erythraea*. Common myrrh (or hirabol myrrh) is obtained from *C. myrrha* (Nees) Engl. Abyssinian myrrh is obtained from *C. madagascariensis* Jacq. (*C. abyssinica*). Other species sometimes passing as myrrh or bdellium include *C. africana* (A. Rich.) Engl., *C. anglosomaliae* Chiov., *C. gileadensis* (L.) Christ. (*C. opobalsamum* (L.) Engl., *C. hildebrandtii* Engl., *C. kataf* (Forsk.) Engl., *C. molmol* Engl. ex Tschirch (Somalian myrrh), *C. mukul* (Hook.) Engl., and *C. schimperi* (Berg) Engl. Myrrh has been employed for incense and embalming since ancient times. Myrrh is employed by perfumers as an absolute, oil, or resinoid. Myrrh is included in the formulations of a number of modern perfumes, is used by many herbalists as an astringent for the mucous membranes of the mouth and throat.

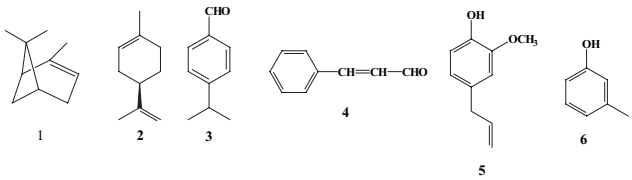
Myrrh

As mentioned by Guenther[4], myrrh (also called heerabol-myrrh or bitter myrrh) is gum-resin obtained from several species of *Commiphora* (fam. *Burseraceae*), notably *C. abyssinica* (Berg) Engler, *C. schimperi* (Berg) Engler, and *C. myrrha* (Nees) Engler var *molmol* Engler. Genus *Commiphora* comprises more than 200 species, all native to Africa, Arabia, Madagascar and India.

In order to collect gum, the natives make incisions into the bark, causing the exudation of a yellowish oleoresin. Exposed to the air, this dries, hardens and turns reddish-brown.

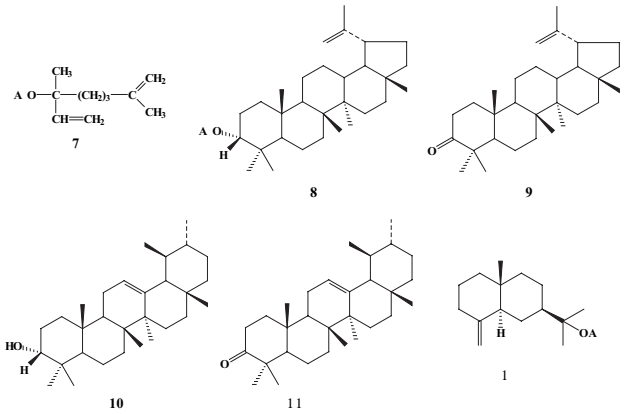
Myrrh is partly soluble in ethanol (~ 30 % alcohol-soluble material) and is also partly soluble in water and in ether. Since antiquity myrrh has served as a constituent of incense. Oil of myrrh is a valuable ingredient in perfumes (balsamic, heavy odour).

The chemistry of myrrh oil was first investigated by Lewinsohn (Arch. Pharm. 244, 412, 1906), von Friedrichs (Arch. Pharm. 245, 432, 1907) and Trost and Doro (Ann. chim. Applicata 26, 126, 1936). These authors found the following constituents: α-pinene **1**, dipentene [= (±)-limonene], limonene **2**, cuminaldehyde **3**, cinnamic aldehyde **4**, eugenol **5**, m-cresol **6**, heerabolene (probably tricyclic sesquiterpene), cadinene (?), a sesquiterpene (?), a bicyclic sesquiterpene ($C_{15}H_{24}$), a tricyclic sesquiterpene ($C_{15}H_{24}$), formic acid, acetic acid, myrrholic acid (?, $C_{16}H_{21}O_3$.COOH) and palmitic acid.

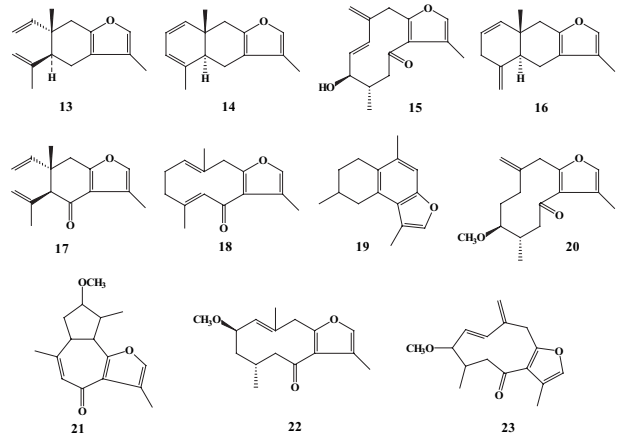


1 2 3 4 5 6

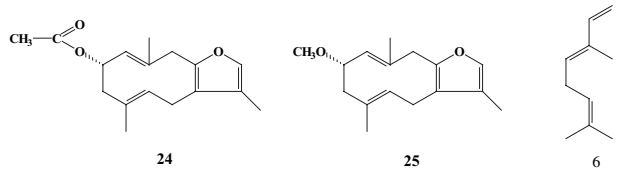
Later was from "*Commiphora* myrrha" resin isolated the following compound – isolinalyl acetate **7**, 3-epi-lupenyl acetate **8**, lupeone **9**, 3-epi-α-amirin **10**, α-amirone **11**, acetyl β-eudesmol **12** and a sesquiterpenoid lactone[5].



Another laboratory reported on the following in oil of myrrh[6]: 11.9% curzerene **13** (ref.[7-10]), 12.5% furanoeudesma-1,3-diene **14**, 1.2% 1,10(15)-furanodien-6-one **15** (ref.[11, 12]), 3.5% lindestrene **16** (ref.[13-15]), 11.7% curzerenone **17** (ref.[16, 17]), 0.4% furanodien-6-one **18**, 1.1% dihydropyrocurzerenone **19**, 1.5% 3-methoxy-10(15)-dihydrofuranodien-6-one **20**, 0.1% 3-methoxyfuranoguaia-9-en-8-one **21**, 0.2% 2-methoxy-4,5-dihydrofuranodien-6-one **22**, and 0.9% 3-methoxy-10-methylenefuranogermacra-1-en-6-one **23**. These authors also reported that a mixture of furanoeudesma-1,3-diene and lindestrene possessed a typical myrrh odor, while dihydropyrocurzerenone possessed a resinous myrrh odor; the latter compound best represented the odor of myrrh by itself.



2-acetoxyfuranodiene **24** and 2-methoxyfuranodiene **25** were isolated from chloroform extract of ground myrrh (commercially available) with the help of flash chromatography by Monti[18]. The absolute configuration of these compounds was determined.



Ma et al. (ref.[19]) described an analytical supercritical fluid extraction (SFE) system and its application to GC/MS of frankincense and myrrh, Chinese medicines. The result shows that analytical SFE is a more afficient technique for investigating Chinese medicine compounds. In addition the information generated supplements to the available literature on title medicines and revealed its potential application in the compound study of the Chinese herbal medicine.

The constituents of the supercritical fluid extraction and the steam distillate of myrrh and *Curcuma zedoaria*, two Chinese herbal medicines with the help of GC/ITD studied Yu[20]. Fourty one and 45 compounds were identified, respectively, in myrrh and *C. zedoaria* which were mainly sesquiterpenoids and furanose sesquiterpenoids. The feature of their ion trap mass spectrum is also discussed.

The purity of myrrh batches of various origin were tested according to the DAB 10 (10th German pharmacopeia)[21]. The contents and structures of the gum fractions were identical despite differences in the essential oil fractions. The raw gums were heterodisperse systems and contained ~70% 4-methyl-glucuronogalactone protein. Therefore, a classification of myrrh in the group of arabinogalactan proteins is no longer correct.

Wang[22] analyzed by capillary GC/MS and GC/FTIR the chemical components of the essential oil of myrrh obtained from Kenya. The oil contained monoterpenes and sesquiterpenes. Researchers identified sixteen main constituents.

The constituents of essential oil in myrrh and gum opopanax were analyzed by GC-MS. Fifteen compounds in Myrrh and 33 compounds in gum opopanax were identified and their percent content was detected. The main constituents of myrrh was furanoeudesma-1,3-diene **14** and the main constituent of gum opopanax was *trans*-β-ocimene **26** (ref.[23]).

With the help of Fourier-transform Raman spectroscopy myrrh can be easily distinguished from frankincense and different colored specimens can be identified. Relative proportions of compounds in a sample, and hence the color, is dependent on the climatic and environmental conditions. Myrrh shows more variety in its color (myrrh red, myrrh orange, myrrh yellow, myrrh brown and myrrh black) and in the observed Raman spectra. The common bands which occur for myrrh samples are not specific enough for identification of individual colored myrrh samples[24]. Such non-destructive methods of analysis are preferred by archeologists.

Tree resins have been used extensively throughout history. Tree resins are composed of terpene and terpenoid compounds, and diterpenoids and triterpenoids are the most common. Diterpenoids and triterpenoids have not been found together in a resin; thus, resins from each group have differing properties. Frankincense and myrrh are resins that contain triterpenoid components. Fourier transform-Raman spectrometry has potential as a non-destructive and noninvasive means of identifying both ancient and modern resin samples *in situ*. Because of that it has advantages particularly in the field of archeological sciences. The spectra of myrrh are very different than those of any of the other resins examined. Myrrh

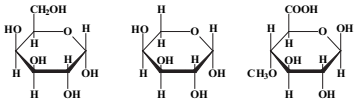
cannot be mistaken for any other resin because it has a high enough proportion of gum to make its spectra unlike those of any of the resins examined by the authors. The spectra of myrrh are easily distinguished from those of the diterpenoid and triterpenoid resins[25].

Commiphora myrrha

The isolation and characterization of D-galactose **27**, L-arabinose **28**, and 4-methyl D-glucuronic acid **29** as component of gum myrrh (*Commiphora myrrha* Holmes) are described.

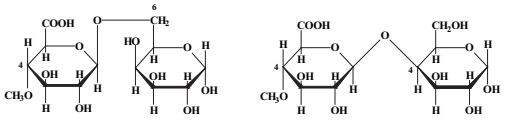
The gum myrrh has been used as incense for many centuries. In more recent times, the gum has found medical usage as an antiseptic, the tincture being applied to inflammatory and ulcerated conditions of the throat and mouth.

Extraction with 90% aqueous alcohol the resins are largely removed and the crude polysaccharides are obtained. After hydrolysis at least 15 aminoacids were detected and in fractions D-galactose, L-arabinose, and 4-methyl D-glucuronic acid (in proportions 4 : 1 : 3) were identified[26].



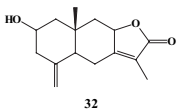
27 **29**

Hydrolysis of purified polysaccharides of gum myrrh (*Commiphora myrrha* Holmes) gave high yields of a mixture of neutral sugars and acidic oligosaccharides. The latter after isolation and purification gave 1:6 mixture of two aldobiuronic acids, identified as 6-O-(4-O-methyl-β-D-glucuronosyl)-D-galactose **30** and 4-O-(4-O-methyl-α-D-glucuronosyl)-D-galactose **31** (ref.[27]).



30 **31**

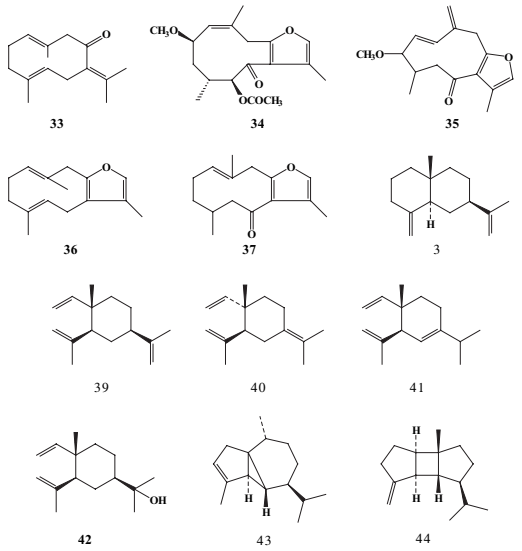
From *Commiphora myrrha* sesquiterpen commiferin **32** was isolated[28].



32

Chromatography of hexane extracts of *Commiphora erythraea* Engler gum, the source of opopanax oil, led to isolation and identification of known furanodienone **18**. The same extraction of *Commiphora myrrh* (Nees) Engler, the source of myrrh oil, resulted in two new furanosesquiterpenoids, 2-O-acetyl-8,12-epoxygermacra-1(10),4,7,11-tetraene **24** and 2-O-methyl-8,12-epoxygermacra-1(10),4,7,11-tetraene **25** (ref.[29]). Both gums were collected in Kenya.

The eight samples of resin collected in Kenya and attributed to *Commiphora myrrha* (one of them called *C. ellenbeckii*) and *Commiphora holtziana* have been examined. These have yielded a wide range of sesquiterpenes, notably furanosesquiterpenes based on eudesmane, elemane and germacrene (Table 1). The distribution of these compounds is discussed in relation to the collection and commerce of myrrh-like resins in Kenya. The simple sesquiterpenes identified in *C. holtziana* were comparable to those recorded for opopanax oil[30].



33 **34** **35**

36 **37** 3

39 40 41

42 43 44

Table 1. Major sesquiterpenes identified from *Commiphora myrrha* and *C. holtziana*.

Components	*C. myrrha*	*C. holtziana*
germacrone[a] **33**	+	+
C **22**	–	+
D **34**	–	+
B **35**	–	+
furanodiene[b, c] **36**	+	–
2-methoxyfuranodiene **25**	+	–
4,5-dihydrofuranodiene-6-one **37**	+	+
β-selinene **38**	–	+
lindestrene **16**	+*	+
furanoeudesma-1,3-diene **14**	+	–
β-elemene **39**	+	+**
γ-elemene **40**	+	+
δ-elemene **41**	–	+
elemol **42**	–	+
isofuranogermacrene[c] **13**	+**	–
curzerenone **17**	+	+
α-cubebene **43**	+	–
β-bourbonene **44**	–	+

* found in all samples, ** found in most of the samples

a[31, 32], b[33], c[9]

B = (1E)-3-methoxy-8,12-epoxygermacra-1,7,10,11-tetraen-6-one

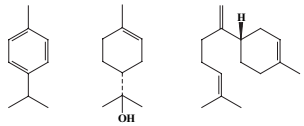
C = (1(10)E,2R*,4R*)-2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one

D = *rel*-2R-methyl-5S-acetoxy-4R-furanogermacr-1(10)Z-en-6-one

Gum resins of *Commiphora myrrha* (Nees) Engler are important commercial products (fragrant oil) in Kenya, Ethiopia and Somalia. Hexane-soluble viscosous oil is responsible for the characteristic odor of the gum. With the help of high-performance liquid chromatography the oil mixture was separated into pure compounds. These were identified with GC/MS as known furanosesquiterpenoids isofuranogermacrene (= isogermafurene) **13**, lindestrene **16**, furanoeudesma-1, 3-diene **14** and furanodiene (= isofuranodiene) **36**. Based on the presence or absence of these compounds, it is possible to differentiate or detect adulteration of commercial gum resins labeled as *C. myrrh* myrrh oil from *C. erythraea* opopanax oil[34].

The best quality of myrrh is obtained from the species *Commiphora myrrha* (Nees) Engl. This myrrh one can find also under synonyms *C. rivae* Engl, *C. coriacea* Engl., *C. molmol* (Engl.) Engl. and *C. habessinica* (Berg.) Engl. var. *grossedentata* Chiov. Myrrh is collected from other species of *Commiphora* as well. These include: *C. Africana* (A. Rich.) Engl., *C. erythraea* (Ehrenb.) Engl., *C. gileadensis* (L.) C. Chr., *C. habessinica* (Berg) Engl., *C. hodai* Sprague, *C. kua* (R. Br. Ex Royle) Vollesen, *C. quadricinta* Schweinf., *C. schimperi* (Berg) Engl. and *C. truncate* Engl.

Chemical investigation of *Commiphora* has been done on some Kenyan species occurring also in Ethiopia. The main volatile components include monoterpenes (limonene **2**, p-cymene **45**, α-terpineol **46**) and sesquiterpenes (β-bisabolene **47**)(ref.[35]).



45 46 47

A furanoeudesmane, 5αH-8,12-furanoeudesma-1,3-diene (furanoeudesma-1,3-diene) **14**, was synthetised[36]. A natural product isolated first from *Commiphora molmol* and later from *Commiphora myrrh* oil was synthetised enantiomerically pure.

The resin of *Commiphora myrrha*, collected in Ethiopia, was extracted with aqueous ethanol and petroleum ether. Following partition and column chromatography gave previously reported antihyperglycemic compounds, furanoeudesma-1,3-diene **14** and 2-O-acetyl-8,12-epoxygermacra-1(10),4,7,11-tetraene **24** (ref.[37]).

Commiphora myrrha Engl., a plant found in some African and Asian countries (as Kenya, India or People's Republic of China), yields a yellow nonvolatile gum resin (myrrh), which has been used as a food additive, a fragrance, and a traditional medicine. Authors here reported isolation of two new sesquiterpenoids as well as four known derivatives from a Chinese sample of *C. myrrha*. After exudates extraction with ethyl acetate and column chromatography on silica gel four already known compounds were eluted, namely curzerenone **17**, furanogermacra-1(10)Z,4Z-dien-6-one **48**, *rel*-3R-methoxy-4S-furanogermacra-1E,10(15)-dien-6-one **49** and

Table 2. Relative concentration (%) of components of the hydrodistillates of *Commiphora sphaerocarpa*, *C. holtziana*, *C. kataf* and *C. myrrha* (GC-MS).

Components	*C. s.*	*C. h.*	*C. k.*	*C. m.*
α-pinene **1**	0.6	–	–	–
myrcene **52**	1.5	–	–	–
δ-elemene **41**	–	–	0.4	2.1
α-copaene **53**	5.3	1.1	tr	0.2
β-bourbonene **44**	–	–	0.7	1.2
β-ylangene **54**	–	–	–	0.3
β-elemene **39**	6.7	5.0	6.4	8.7
α-gurjunene **55**	7.0	–	0.5	–
trans-caryophyllene **56**	1.0	–	0.5	1.3
γ-elemene **40**	–	–	–	1.1
α-humulene **57**	0.7	0.4	0.7	0.6
alloaromadendrene **58**	–	–	–	0.2
γ-muurolene **59**	–	–	–	0.2
germacrene D[d] **60**	–	23.0	9.0	3.2
β-selinene **38**	8.0	7.0	2.0	0.6
α-selinene **61**	11.0	–	2.4	0.5
bicyclogermacrene[e] **62**	–	–	–	0.2
α-guaiene **63**	6.0	–	–	–
γ-cadinene **64**	4.7	–	0.3	1.2
δ-cadinene **65**	2.1	1.1	1.0	0.4
furanodiene **36**	–	–	–	19.7
isofuranogermacrene **13**	–	–	–	2.0
elemol **42**	–	–	–	0.2
germacrene-B **66**	5.0	7.2	7.1	4.3
furanoeudesma-1,4-diene **67**	–	–	–	1.2
furanoeudesma-1,3-diene **14**	–	–	–	34.0
lindestrene **16**	–	–	–	12.0
β-eudesmol **68**	–	–	2.0	–
T-cadinol **69**	7.0	–	–	1.6
2-methoxyfuranodiene **25**	–	–	–	2.1
2-acetoxyfuranodiene **24**	–	–	–	tr
curzerenone **17** furanodienone **18**	13.0	6.1	1.0	–
germacrone **33**	1.0	2.0	3.0	–
A **51**	2.0	11.4	22.0	–
dihydropyrocurzerenone **19**	1.2	–	3.4	–
B **35**	2.4	1.0	tr	–
C **22**	3.0	3.1	13.0	–

d[40,41], e[42,43]

A = (1E)-8,12-epoxygermacra-1,7,10,11-tetraen-6-one

B = (1E)-3-methoxy-8,12-epoxygermacra-1,7,10,11-tetraen-6-one

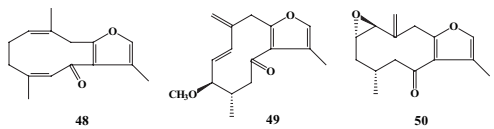
C = (1(10)E,2R*,4R*)-2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one

Table 3. Relative concentration (%) of components in Commiphora myrrha var. molmol essential oil.

Compound	%
δ-elemene **41**	0.5
β-bourbonene **44**	0.6
β-elemene **39**	8.4
β-caryophyllene **56**	0.7
γ-elemene **40**	2.6
α-humulene **57**	0.3
dehydroaromadendrane **70**	0.1
9-*epi*-caryophyllene **71**	0.4
γ-muurolene **59**	0.3
alloaromadendrene **58**	1.7
curzerene **13**	40.1
γ-cadinene **64**	0.8
δ-cadinene **65**	0.3
β-sesquiphellandrene **72**	0.2
selina-3,7(11)-diene **73**	0.2
elemol **42**	0.2
caryophyllene alcohol **74**	0.4
caryophyllene oxide **75**	0.2
cis-β-elemenone **76**	0.8
furanoeudesma-1,3-diene **14**	15.0
γ-eudesmol **77**	2.7
furanodiene **36**	1.1
7-*epi*-α-eudesmol **78**	2.2
2-O-methyl-8,12-epoxy- germacra-1(10),4,7,11-tetraene, isomer I* **25**	0.5
2-O-methyl-8,12-epoxy- germacra-1(10),4,7,11-tetraene, isomer II* **25**	3.9
2-hydroxyfuranodiene **79**	0.2
10-*epi*-γ-eudesmol acetate **80**	0.3
2-O-acetyl-8,12-epoxy-germacra-1(10),4,7,11-tetraene, isomer I* **24**	6.5
2-O-acetyl-8,12-epoxy-germacra-1(10),4,7,11-tetraene, isomer II* **24**	0.3

* correct isomeric form was not determined

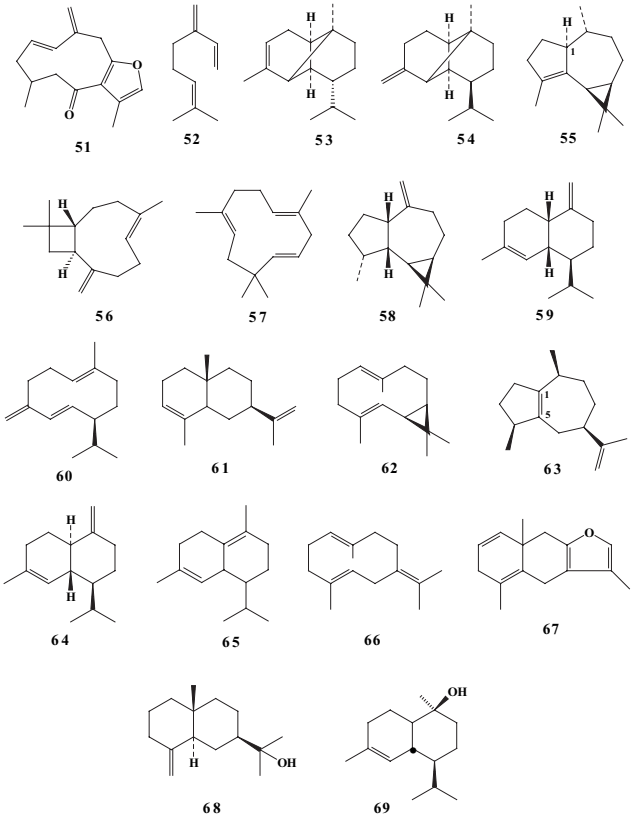
rel-2R-methoxy-4R-furanogermacr-1(10)E-en-6-one **22**. The structures of the new compounds, *rel*-1S,2S-epoxy-4R-furanogermacr-10(15)-en-6-one **50** and *rel*-2R-methyl-5S-acetoxy-4R-furanogermacr-1(10)Z-en-6-one **34**, were elucidated by spectroscopic methods and with the aid of molecular modeling[38].



48 49 50

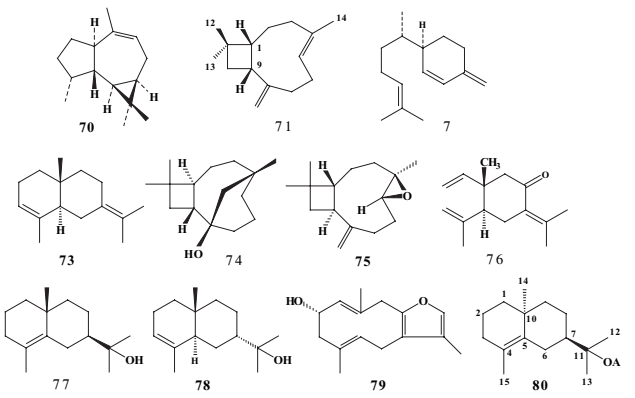
The genus *Commiphora* comprises over 150 species, most of which are confined to Eastern Africa, with few species also occurring in Arabia and India. The composition of true myrrh, derived from *C. myrrha* was compared with some of its adulterans (*C. sphaerocarpa* Chiov., *C. holtziana* Engl. and *C. kataf* (Forssk. Engl.) (Table 2). The petrolether extract of *C. sphaerocarpa* gave after chromatography over silica six compounds. One of them, (1E)-8,12-epoxygermacra-1,7,10,11-tetraen-6-one **51**, is a new furanosesquiterpene[39].

Analysis of true myrrh failed to confirm presence of curzerenone, furanodienone, (1E)-3-methoxy-8,12-epoxygermacra-1,7,10,11-tetraen-6-one and (1(10)E,2R*,4R*)-2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one.



51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69

Hydrodistillation of the crushed air-dried oleo-gum resin of *Commiphora myrrha* (Nees) Engl. var. *molmol* yielded 3.1 % of oil. The chemical composition of the essential oil was examined using GC and GC/MS (Table 3). The relative percentage of the 32 compounds (about 94.6 % of the oil) identified in this oil was calculated from the total ion chromatogram[44].



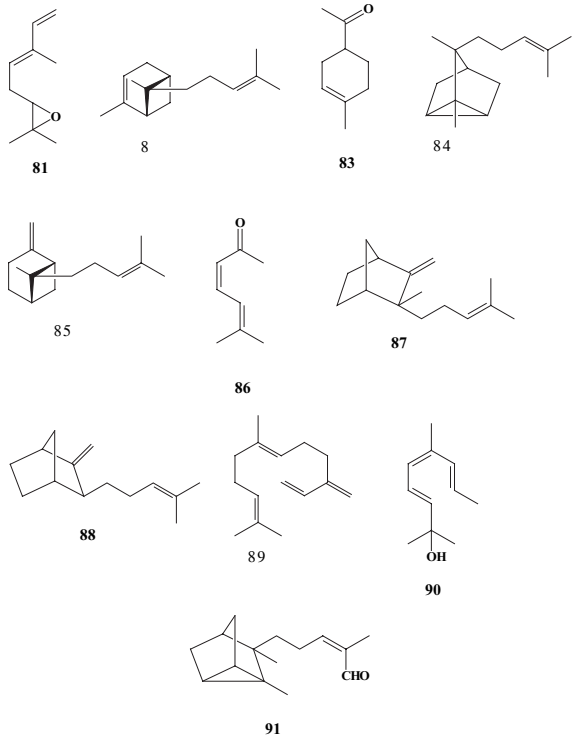
70 71 7 73 74 75 76 77 78 79 80

Table 4. The composition of Ethiopian *Commiphora* essential oils.

Compound	*C. myrrha*	*C. guidotti*
limonene **2**	–	0.2
(Z)-β-ocimene **26**	–	0.7
(E)-β-ocimene **26**	–	33.0
δ-elemene **41**	2.1	–
α-copaene **53**	0.2	–
(E)-β-ocimene epoxide **81**	–	0.3
β-bourbonene **44**	1.2	–
cis-α-bergamotene **82**	–	0.3
1-methyl-4-acetylcyclohex-1-ene **83**	–	0.5
β-ylangene **54**	0.3	–
α-bergamotene **82**	–	3.0
α-santalene **84**	–	15.8
trans-β-bergamotene **85**	–	6.6
β-elemene **39**	8.7	0.1
6-methyl-3,5-heptadiene-2-one **86**	–	0.4
β-caryophyllene **56**	1.3	–
epi-β-santalene **87**	–	0.6
γ-elemene **40**	1.1	–
alloaromadendrene **58**	0.2	–
(Z)-β-santalene **88**	–	0.4
nonanol	–	0.2
(Z)-β-farnesene **89**	–	0.8
(E)-β-farnesene **89**	–	0.8
α-humulene **57**	0.6	–
γ-muurolene **59**	0.2	–
germacrene D **60**	3.2	1.6
cis-α-bisabolene **99**	–	22.2
β-selinene **38**	0.6	–
α-selinene **61**	0.5	–
bicyclogermacrene **62**	0.2	–
decanol	–	1.2
δ-cadinene **65**	0.4	0.2
γ-cadinene **64**	1.2	–
2,6-dimethyl-3(E),5(E),7-octatrien-2-ol **90**	–	0.7
germacrene B **66**	4.3	–
furanodiene **36**	19.7*	0.1
elemol **42**	0.2	–
furanoeudesma-1,4-diene **67**	1.2	–
furanoeudesma-1,3-diene **14**	34.0*	–
lindestrene **16**	12.0*	–
T-cadinol **69**	1.6	–
(E)-α-santalal **91**	–	0.4
2-methoxyfuranodiene **25**	2.1	–

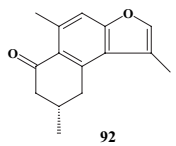
* Confirmed by co-injection and NMR.

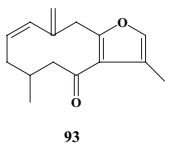
Most previous reports were based on materials obtained from markets rather than from properly identified trees. Authors here described the results on the volatile oils (obtained by hydrodistillation) of resin collected in Ethiopia from two *Commiphora* spp. (*C. myrrha* and *C. guidotti*). The oils were analysed by GC/MS (Table 4). Using ^{1}H- and ^{13}C and GC/MS analysis authors established in their previous work the absence of oxygenated furanosesquiterpenes, curzerenone and furanodienone, and other C-6 oxygenated furanosesquiterpenes in the essential oil as well as extracts of myrrh[45]. The source of adulterant resins coming mainly from *C. sphaerocarpa*, *C. holtziana* and *C. kataf.*

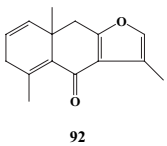


Ethyl acetate extract of an exudate of *Commiphora myrrha*, which had been collected in People's Republic of China, was separated by column chromatography on silica gel and RP-18 (ref.[46]). From collected fractions seven compounds (aromatic sesquiterpenes) were isolated and identified – myrrhone **92** (a weak floral with relatively strong animal-like note; a new sesquiterpene), epicurzerenone **48** (with the same odour as the previous one), furanogermacra-1*E*,10(15)-dien-6-one **93**, 2-methoxy-furanogermacra-1(10),4-diene **25** (a slightly floral and weak leathery odour), T-cadinol **69** (very interesting animal and castoreum-like odour quality), 3α-hydroxy-T-cadinol **219** (a slightly leathery odour), and a well-known sesquiterpene, eudesm-4(15)-ene-1β,6α-diol **222** (the same odour quality as T-cadinol).

The structures of these compounds were determined on the basis of spectral data, especially of NMR evidence (^{1}H- and ^{13}C-NMR spectra) and with the help of positive atmospheric pressure chemical ionization mass spectra (APCI MS) and electrospray ionization mass spectra (ESI MS).


92


93

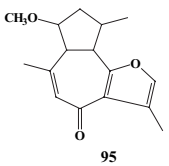

92

Commiphora molmol

From the hexane extract of the essential oil of myrrh, *Commiphora molmol* Engler, three new furanogermacrenes (2-methoxy-4,5-dihydrofuranodiene-6-one **22** – $C_{16}H_{22}O_3$, 5-acetoxy-2-methoxy-4,5-dihydrofuranodiene-6-one **34** – $C_{18}H_{24}O_5$ and 3-methoxy-10-methylene-furanogermacra-1-ene-6-one **49** – $C_{16}H_{20}O_3$) have been with the help of column chromatography isolated and their structures elucidated[47].

The non-polar fraction of hexane extract of myrrh, the resin of *Commiphora molmol* Engler, gave on column chromatography as the main compound the new furanoeudesmane, furanoeudesma-1,3-diene **14**. Another isolated compounds were α-copaene **53**, bourbonene **44**, furanodiene **36**, β-elemene **39** and furanoeudesmane lindestrene **16**. From the polar fraction of the essential oil another new furanosesquiterpene of the eudesmane type was isolated by liquid chromatography, furanoeudesma-1,4-diene-6-one **94**, besides curzerenone **17** and furanodiene-6-one **18** (ref.[48]).

From the fractionated essential oil of myrrh, *Commiphora molmol*, several compounds were isolated and identified by column chromatography. In addition to 1(10)E,4E-furanodiene-6-one **18** and its *cis*-isomer 1(10)Z,4Z-furanodiene-6-one **18**, which were separated without difficulty, was isolated curzerenone **17** and 2-methoxyfuranoguaia-9-ene-8-one **95**. 2-Methoxyfuranodiene **25** was separated from the accompanying furanoeudesma-1,4-diene-6-one **94**. From an accompanying unidentified furanosesquiterpene ketone was separated 2-acetoxyfuranodiene **24**. The last identified compound was 4,5-dihydrofuranodiene-6-one **37** (ref.[49]).


95

Myrrh, a commercially used resin, is mostly from *Commiphora molmol*, growing wild in Somalia, Jemen and Arabia. It is mainly used in toothpastes and tinctures for treatment of gingivitis. Myrrh is composed of the essential oil (2–10 %), the ethanol soluble resin (25–40 %) and the watersoluble gum (30–60 %). The watersoluble gum fraction of myrrh has been found to comprise of a mixture of proteoglycans (with dominating amounts of uronic acid polymers). After hydrolysis and degradations structural investigations revealed chains of galactose **27**, chains of arabinose **28** and 4-O-methyl-glucuronic acid **29** ("4-O-methyl-glucurono-galactan"), arabino-3,6-galactan-protein fractions and protein. Authors studied sugar and amino acid compositions of the fractions and sugar linkages of the fractions. Partial structure of the fractions was proposed. The covalent binding of protein and carbohydrate moiety is most probable. In the crude gum the two aldobiuronic acids 6-O-(4-O-methyl-D-glucuronosyl)-D-galactose **30** and 4-O-(4-O-methyl-D-glucuronosyl)-D-galactose **31** were identified (ratio 6 : 1)(ref.[50]). It is not sure, whether the different proteoglycans represent different polymers resulting from the biosynthesis sequence or whether they derive from a partial degradation during isolation or storage of myrrh.

In antiquity, myrrh was used by the Egyptians for embalming and by the Jews as anointing oil. In St Mark's Gospel, "vinum murratum", wine with myrrh, was offered to Christ before crucifixion. Hexane extract of *Commiphora molmol* with analgesic activity was separated by silica gel column chromatography and semi-preparative HPLC. From the three identified sesquiterpenes the most abundant compound was furanoeudesma-1,3-diene **14** (> 90 %). The other compounds were isofuranogermacrene **13** and furanodiene **36**. The first two compounds were analgesic[51].

The non-polar fraction of myrrh resin from *Commiphora molmol* was extracted with hexane. This extract was separated by column chromatography. With a combination of mass spectrometry and ^{1}H-NMR were characterized different fractions. These gave eight sesquiterpene fractions, namely 1, furanodiene **36**, furaneudesma-1,3-diene **14** and curzerene **13**; 2, methoxyfuranodiene **25**; 3, acetoxyfuranodiene **24**; 4, curzerenone **17**; 5, furanodiene-6-one and methoxyfuranoguaia-9-ene-8-one **95**; 6, furanogermacrene-3 **49**; 7, furanogermacrene-1 **22** and fraction 8, furanogermacrene-2 **34** (ref.[52]). All these compounds had been described previously. The fractions were tested. Fraction 5 (furanodiene-6-one and methoxyfuranoguaia-9-ene-8-one in approximately equivalent amounts) showed antibacterial and antifungal activity against standard pathogenic strains. These compounds also had strong local anaesthetic activity.

Commiphora opobalsamum

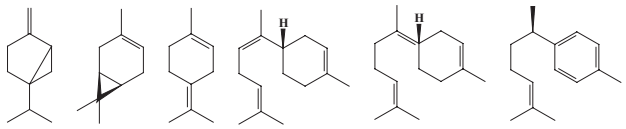
The cardiovascular effects of aqueous extracts from the branches of *Commiphora opobalsamum* (syn. *Commiphora gileadensis* (L.) Engl.), tree from the mountains of Ramallah, were investigated. The intravenous administration of 4 mg/kg of the aqueous extract depressed systemic arterial blood pressure by 20 % ($P < 0.01$) and reduced heart rate of anaesthetised rats by 14 % ($P < 0.05$). The hypotensive and the bradycardiac effects were immediate and in a dose related manner. The hypotensive effect of *C. opobalsamum* was inhibited by the pretreatment with atropine sulfate (1-4 mg/kg). These results suggest that the hypotensive effect of *C. opobalsamum* is due to the activation of muscarinic cholinergic receptors[53].

Opopanax

The monoterpene hydrocarbon composition of 29 essential oils was determined with the help of downward chromatostrip procedure, followed by gas chromato-

graphic analysis identification based on comparison of retention times with known compounds. In one of this commercially available non-citrus essential oils, opopanax (*C. erythrea*), were found almost entirely ocimene **26** with trace amounts of α-pinene **1**, sabinene **96**, Δ^3-carene **97**, myrcene **52**, *d*-limonene **2**, and terpinolene **98** (ref.[54]).

From authentic essential oil of opoponax with the help of column chromatography followed by gas chromatography α-bisabolene **99**, β-bisabolene **47**, and γ-bisabolene **100** were separated[55].



From several commercial essential oils 36 sesquiterpenes were isolated in sufficient quantity, purified by gas chromatography and identified from infrared spectra. When it was possible, the individual sesquiterpene hydrocarbon was isolated from more than one essential oil (21 sesquiterpenes). From opopanax for high resolution infrared spectra were isolated α-bergamotene **82**, β-bisabolene **47**, γ-bisabolene **100** (may be a mixture), γ-cadinene **64**, δ-cadinene **65**, *ar*-curcumene (α-) **101** and α-santalene **84** (ref.[56]).

Regan and Andrews examined samples of oil of opopanax and isolated and identified in it α-santalene **84** and α-bisabolene **99** (ref.[57]). They did not find any β-bisabolene and γ-bisabolene.

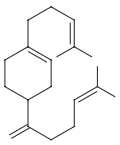
Another scientific team re-examined their samples following column and gas chromatographic purification and concluded that oil of opopanax contains α-santalene **84**, α-bisabolene **99** and β-bisabolene **47**, as well as some other isomeric bisabolene[58].

The sesquiterpenes of opopanax oil were studied. Opopanax oil (also called bisabol myrrh) is obtained by the steam distillation of the natural oleo-gum-resin from the tree *Commiphora erythrea glabrascens* Engler. During this study, trans-β-ocimene **26** was confirmed as the major monoterpenic hydrocarbon constituent and 18 additional sesquiterpenes were identified. The five major sesquiterpene hydrocarbon constituents were identified as *cis*-α-bergamotene **82**, α-santalene **84**, *trans*-α-bergamotene **82**, *trans*-α-bisabolene **99**, and β-bisabolene **47**. Between another 13 were δ-elemene **41**, α-cubebene **43**, α-copaene **53**, β-elemene **39**, caryophyllene **56**, γ-elemene **40**, *epi*-β-santalene **87**, β-santalene **88**, humulene **57**, γ-muurolene **59**, *ar*-curcumene **101**, γ-cadinene **64**, and δ-cadinene **65** (ref.[59]).

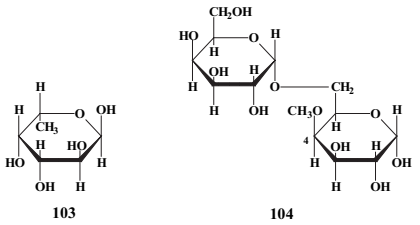
For revision of the configuration of natural (+)-α-bisabolene from opopanax oil were stereospecifically syntetised (E)- and (Z)-α-bisabolenes. Whilst (Z)-α-bisabolene remotely recalls the typical odour of Opopanax, there is no trace of it in (E)-bisabolene. Authors also isolated α-bisabolene from the oil of opopanax. After purification it was identical with (+)-(S, Z)-α-bisabolene **99** (ref.[60]).

Commiphora mukul

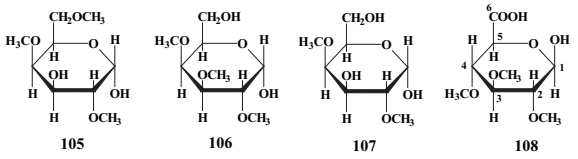
The gum-resin of *Commiphora mukul* furnishes essential oil (~ 0.4 %) consisting chiefly of myrcene **52** and "dimyrcene" (camphorene **102**) were isolated[61].



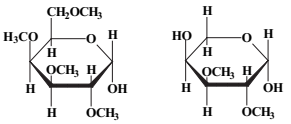
Composition of the gum resin from *Commiphora mukul* (syn. *Balsamodendron mukul* Hook ex Stocks), commonly known as "guggul", was studied. Complete hydrolysis of the gum revealed the presence of L-arabinose **28**, D-galactose **27**, L-fucose **103**, 4-O-methyl-D-glucuronic acid **29** and aldobiouronic acid (built up of D-galactose and 4-O-methyl-D-glucose) **104** (ref.[62]).



The degraded gum of *Commiphora mukul* gave after acid hydrolysis an aldobiouronic acid, 6-O-(4-O-methyl-β-D-glucopyranosyluronic acid)-D-galactose alone with D-galactose. The degraded gum prepared by the autohydrolysis was converted into its fully methylated derivative. Methanolysis and subsequent acid hydrolysis of the methylated polysaccharide furnished neutral and acidic sugar fraction. Paper chromatographic separation of the neutral fraction furnished three sugars, namely 2,4,6-tri-O-methyl-D-galactose **105**, 2,3,4-tri-O-methyl-D-galactose **106** and 2,4-di-O-methyl-D-galactose **107** and an acidic sugar fraction gave 2,3,4-tri-O-methyl-D-glucuronic acid **108** (in the ratio 1 : 6 : 2 : 3). It was established that the degraded gum is a branched polysaccharide[63].

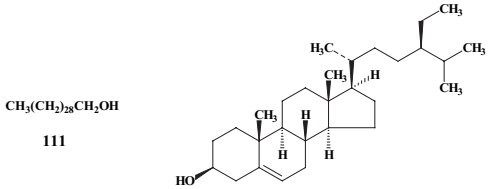


Hydrolysis of methylated *Commiphora mukul* gum furnished 2,3,4,6-tetra-O-methyl-D-galactose **109**, 2,3-di-O-methyl-L-arabinose **110**, 2,3,4-tri-O-methyl-D-galactose **106**, 2,4-di-O-methyl-D-galactose **107** and 2,3,4-tri-O-methyl-D-glucuronic acid **108** in the ratio 1:1:1:2:1. The provisional structure advanced shows the gum to be a highly branched polysaccharide[64].



109 110

The *Commiphora mukul* was extracted with alcohol and the extract, after removal of the solvent, was partitioned between water and ether. Two crystalline compounds were isolated from the unsaponifiable portion of the ether-soluble residue and identified as myricyl alcohol **111** (m.p. 83-4°) and β-sitosterol **112** (m.p. 137-8°)(ref.[65]). The aqueous fraction was chromatographed by a 2-dimensional method using buthanol-acetic acid-water (100:22:50) as the solvent mixture and ninhydrin as the developing agent. The amino acids cystine, histidine, lysine, arginine, aspartic acid, serine, glutamic acid, threonine, alanine, proline, thyrosine, tryptophan, valine, leucine, and isoleucine were detected.

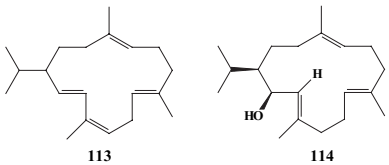


111 11

With the help of column chromatography of petroleum ether extract of *Commiphora mukul* a crystalline needles were isolated[66]. An isolated compound (steroid) showed significant anti-inflammatory activity on rat paw edema produced by carrageenin. The activity is dose dependent and much more potent than the resin fraction present in *C. mukul*.

The compound was found to be three times more potent than the resin fraction isolated from the same drug in inhibiting carrageenin oedema in rats. In the present study was tested efficacy of this compound in a chronic model of inflamation in rats. It looks that this drug is likely to be therapeutically effective as anti-inflammatory or anti-rheumatic drug[67].

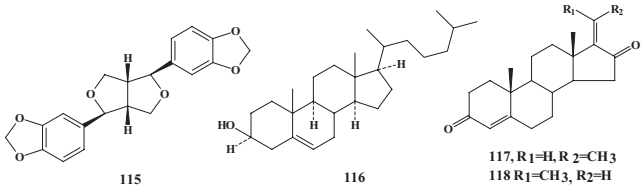
Myrcene **52**, the monocyclic diterpenoids α-camphorene **102** and cembrene **113** were isolated from gum resin of *Commiphora mukul* Engl (Indian gum gugul). For the diterpene alcohol allylcembrol **114**, isolated from the overground parts of *C. mukul*, the structure 2-hydroxy-4,8,12-trimethyl-1-isopropyl-3,7,11-cyclodecatriene was proposed[68].



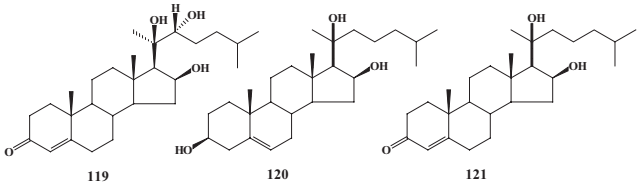
113 **114**

Mukulol (allylcembrol) **114** is a new cembrane alcohol which was isolated from the aerial parts and also from the resin of *Commiphora mukul*[69]. The allylcembrol structure was established by mild dehydration which yielded cembrene and by spectral analysis. Allylcembrol and its C2 epimer were synthetized from isocembrol.

Guggulu (Sanskrit) is the gum resin exudates from the tree *Commiphora mukul* (Hook, ex Stocks) Engl. and is article of commerce in India. Chromatography of petroleum ether soluble fraction gave a diterpene hydrocarbon ($C_{20}H_{32}$), a diterpene alcohol ($C_{20}H_{34}O$), (+)-sesamin **115**, cholesterol **116** and two other new isomeric $C_{21}H_{28}O_2$ steroids, which were identified as 4,17(20)-(*trans*)-pregnadiene-3,16-dione **117** (guggulsterone, Z-isomer) and 4,17(20)-(*cis*)-pregnadiene-3,16-dione **118** (guggulsterone, E-isomer). These two steroids were assigned trivial names, Z- and E-guggulsterone respectively. Ethyl acetate fraction gave additional three new sterols and a long-chain aliphatic triols. The three new sterols have been designated guggulsterol-I **119**, guggulsterol-II **120** and guggulsterol-III **121** (ref.[70]).



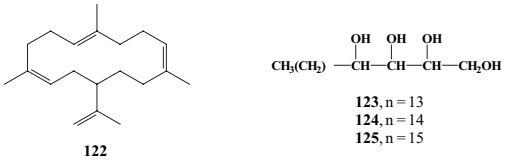
115 **116** **117**, R_1=H, R_2=CH_3 **118** R_1=CH_3, R_2=H



119 **120** **121**

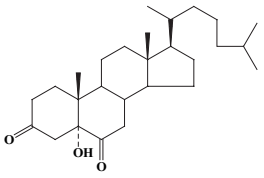
The structures of previously isolated new diterpene hydrocarbon and diterpene alcohol from *Commiphora mukul* were elucidated and named cembrene-A **122** and mukulol **114** (ref.[71]).

As the authors reported before, they isolated from ethyl acetate extract of the gum-resin exudates from the tree *Commiphora mukul* more polar fraction, which yielded colourless prismatic needles of a mixture, now identified as octadecan-1,2,3,4-tetrol **123**, nonadecan-1,2,3,4-tetrol **124** and eicosan-1,2,3,4-tetrol **125** with minor amounts of other components, possibly lower (C_{16}, C_{17}) and higher (C_{21}, C_{22}) homologous tetrols[72]. This was the first reported occurrence of such compounds in nature.



122 **123**, n = 13 **124**, n = 14 **125**, n = 15

Guggulsterol IV **126** and guggulsterol V **127** were isolated from the neutral fraction after saponification of the chloroform extract of guggul gum (*Commiphora mukul*), and their structures were detected by NMR, mass spectra, and chemical modification[73].



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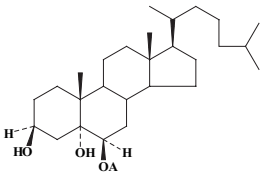


127

Previously described mukulol **114**, a diterpenoid from gum-resin of *Commiphora mukul*, was studied and its absolute stereochemistry established[74].

The stereochemistry of guggulsterol-I, a component of the exudate of Commiphora mukul, was established by a single crystal x-ray difraction analysis to be 20(R), 22(R) (ref.[75]).

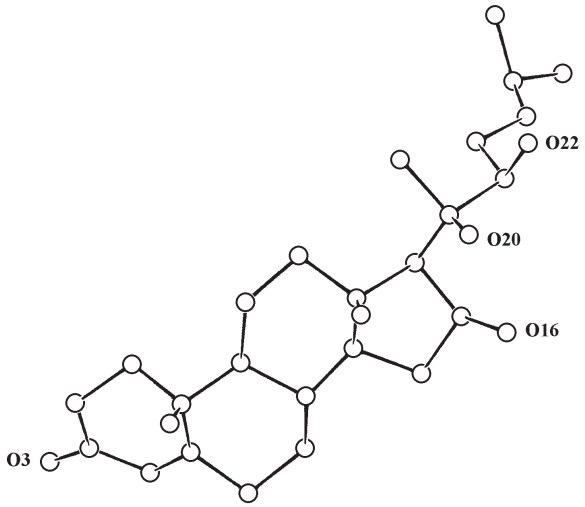
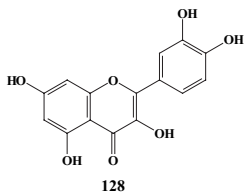


Fig. 1: A computer generated perspective drawing of guggulsterol-I. Hydrogens are omitted for clarity. Adopted by authors.

The major flavonoid components of the flowers of *Commiphora mukul* were identified as quercetin **128**, quercetin-3-O-α-L-arabinoside **129**, quercetin-3-O-β-D-galactoside **130**, quercetin-3-O-α-L-rhamnoside **131**, quercetin-3-O-β-D-glucuronide **132**. The other components were ellagic acid **133** and pelargonidin-3,5-di-O-glucoside **134** (ref.[76]).



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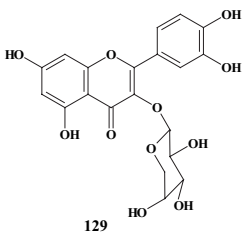

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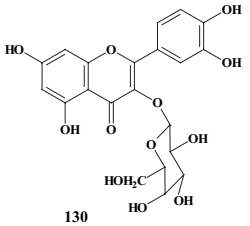

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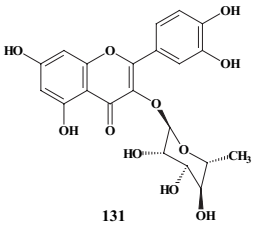

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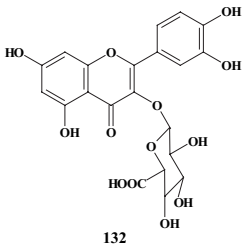

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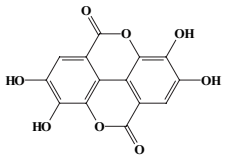

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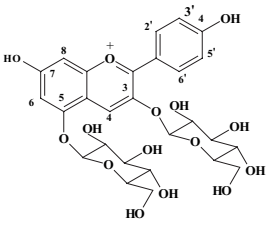
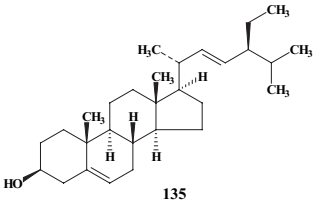


134

The seed oil from *Commiphora mukul* contained linoleic, oleic, stearic and palmitic acids. The unsaponifiable matter contained sitosterol **112**, stigmasterol **135**, cholesterol **116**, campesterol **136**, and α-spinasterol **137** (ref.[77]).



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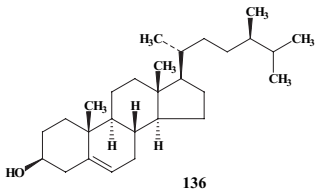

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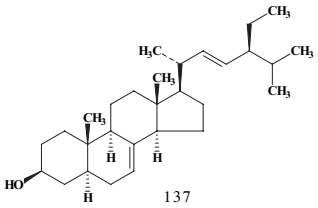
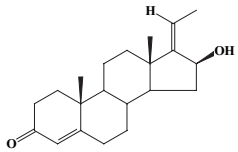


137

Bajaj and Sukh tried to find other minor components from the gum-resin of *Commiphora mukul*. The neutral ethyl acetate soluble fraction was separated on silica gel. A detailed chromatographic analysis of the less polar cut led to the isolation of four C_{21} steroids. Three of these, 16β-hydroxy-4,17(20)Z-pregnadien-3-one **138** (Z-guggulsterol, this compound was reported to occur in nature for the first time), 20α-hydroxy-4-pregnen-3-one **139** and 20β-hydroxy-4-pregnen-3-one **140**, were known compounds. The fourth compound, which is a new naturally occurring C_{21} steroid, has been designated guggulsterol-VI **141** (16-α-hydroxy-4-pregnen-3-one). Stereochemistry at C-20 and C-22 in guggulsterol-I has been clarified[78].



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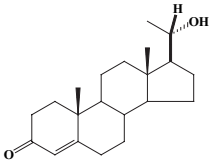

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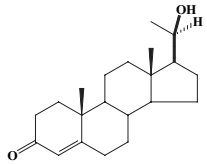

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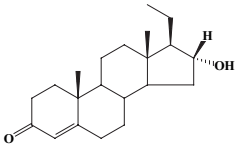
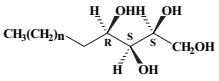


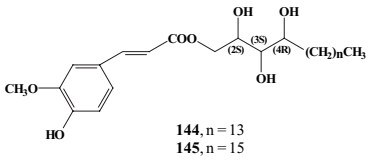
141

Absolute stereochemistry of a new class of naturally occurring lipids named guggultetrols, components of saponified *Commiphora mukul* resin, was elucidated after synthesis of these compounds. The main compound was identified by direct comparison with synthetic compounds as D-xylo (2S, 3S, 4R-configuration), e.g. D-*xylo*-octadecane-1,2,3,4-tetrol (D-*xylo*-guggultetrol-18) **142**. As was already concluded earlier, guggultetrol-20 **143** have the same configuration at the chiral center[79].

With the discovery of the hypolipidemic activity of the gum resin, some chemical investigations have been reported. It was found that guggul resin is a complex mixture of various classes of chemical compounds, such as lignans, lipids, diterpenoids and steroids. From the benzene phase, a waxy solid, which is a mixture of esters based on homologous long chain tetrols and ferrulic acid was identified (**144**, **145**) (ref.[80]).



142, n = 12
143, n = 14

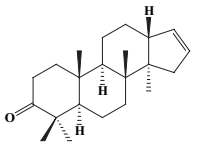


144, n = 13
145, n = 15

A review with 42 references on the development of gum guggulu, a potent hypolipidemic agent, in India, was published[81].

Commiphora wightii (Arnott) Bhand produces an oleo gum resin of several medicinal properties. The plant infected with *Phoma* sp. cause changes in the total chlorophyll (36.65 % decline), soluble sugars (62.77 % reduced) and proteins, phenols (8.1 % increase) and mineral elements (drastic reduction in K^+ and Na^+) in leaf tissues[82].

The resins of *Commiphora mukul* (source of gum guggul in India) and *Commiphora incisa* (a form of frankincense originating from Somalia and Ethiopia) revealed the anti-inflamatory activity. The resins were extracted by steam distillation. Isolated, previously reported, mansumbinone **146** and mansumbinoic acid **147** showed anti-inflammatory effects on oedema and on adjuvant-induced arthritis[83].



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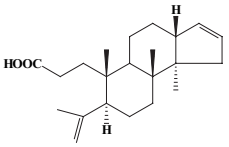
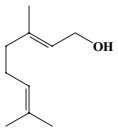


147

The gum resin of *Commiphora mukul* consisted of α-pinene **1**, myrcene **52**, cadinene, geraniol **148**, methylheptanone **149**, eugenol **5**, d-α-phellandrene **150**, d-limonene **2**, (±)-bornyl acetate **151**, 1,8-cineole **152**, (±)-linalool **153**, methylchavicol **154** and α-terpineol **46** (ref.[84]).



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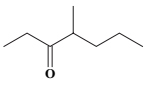

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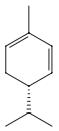

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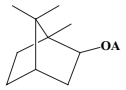

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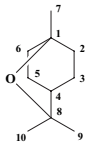

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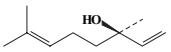

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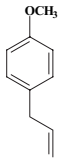
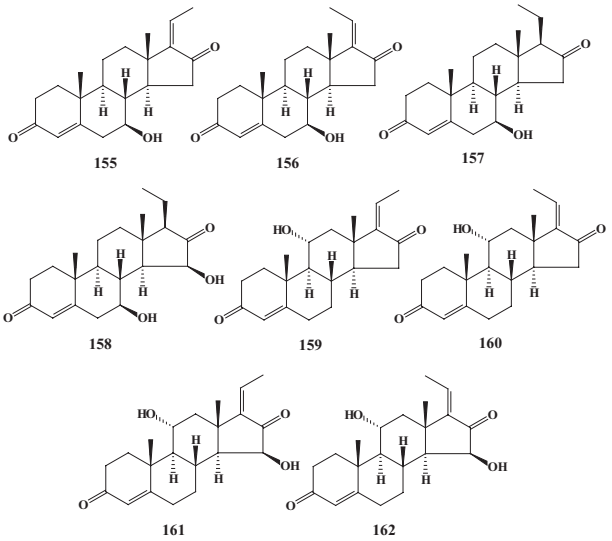


154

A high-performance liquid chromatographic method has been developed and validated for the profiling and quantitative determination of Z- and E-guggulsterones **117**, **118** in *Commiphora mukul* (guggul) crude resin extracts and final products (tablets, capsules), used today as hypocholesterolemic[85].

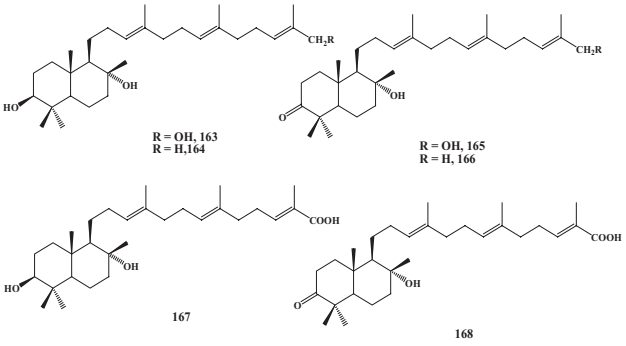
Z- and E-guggulsterone **117**, **118** are the main ingredients of an ayurvedic drug "Guggulip", marketed in India as hypolipidaemic drug. The method was developed for simultaneous determination of these stereoisomers in spiked serum[86]. Lowest quantitation limit was 25 ng/ml. This method was applied for the estimation of this two stereoisomers in rat serum after a single oral dose of Z-isomer. Repeated analysis showed that the Z→E conversion does not take place in the spiked serum samples, and hence the formation of the E-isomer can be attributed solely due to the in vivo process.

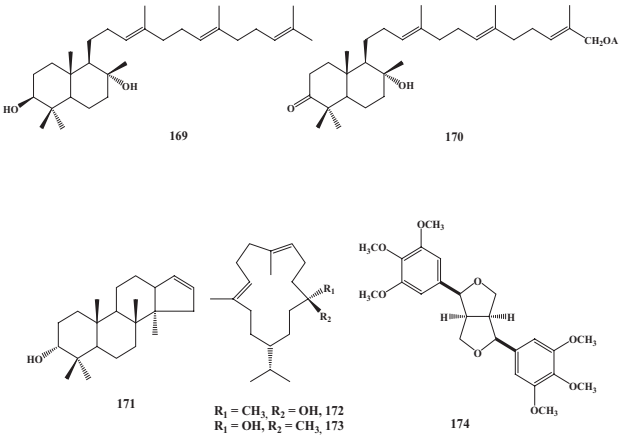
Biotransformation of E-guggulsterone (pregna-4,17(20)-cis-diene-3,16-dione) **118** by *Aspergillus niger* resulted in the formation of four near hydroxyl derivatives identified as 7β-hydroxypregna-4,17(20)-*trans*-diene-3,16-dione **155**, 7β-hydroxypregna-4,17(20)-*cis*-diene-3,16-dione **156**, 7β-hydroxypregn-4-ene-3,16-dione **157**, and 7β,15β-dihydroxypregn-4-ene-3,16-dione **158**. The biotransformation of 1 with *Cephalosporium aphidicola* also resulted in the formation of four new steroidal derivatives as 11α-hydroxypregna-4,17(20)-*trans*-diene-3,16-dione **159**, 11α-hydroxypregna-4,17(20)-*cis*-diene-3,16-dione **160**, 11α,15β-dihydroxypregna-4,17(20)-*trans*-diene-3,16-dione **161**, and 11α,15β-dihydroxypregna-4,17(20)-*cis*-diene-3,16-dione **162**. The structures of these compounds were elucidated on the basis of 1D and 2D NMR spectroscopic techniques[87].



The gum resins of guggul (*Balsamodendron* or *Commiphora mukul* Hook.) are prescribed in India as Ayurvedic folk medicines. Guggul is produced by drying the milky-white sap of the tree for one year. From methanolic extract were isolated five new polypodane-type triterpene compounds, myrrhanols A, B, and C, and myrrhanones A and B, together with three known constituents. Myrrhanol A **163** and myrrhanone A **165** were characterized. Myrrhanol A displays a potent anti-inflammatory effect[88]. The structures and absolute configurations of myrrhanol A and myrrhanone A were determined on the basis of chemical and physicochemical evidence[89].

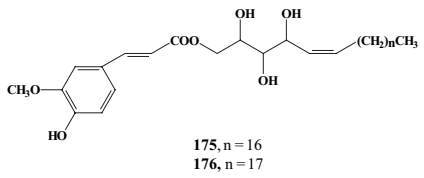
From the methanolic extract from guggul-gum resin, the resin of Commiphora (Balsamodendron) mukul, three new polypodane-type triterpenes, myrrhanol B **167** and myrrhanones B **168** and A acetate **170**, and a new octanordammarane-type triterpene, epimansumbinol **171**, were isolated together with 17 known compounds – myrrhanol A, myrrhanone A, (8R)-3β,8-dihydroxy-polypoda-13E,17E,21-triene (myrrhanol C) **169**, (8R)-3-oxo-8-hydroxy-polypoda-13E,17E,21-triene **166**, 4-pregnene-3,16-dione, 20S-acetyloxy-4-pregnene-3,16-dione, 4,17(20)-(cis)-pregnadiene-3,16-dione, 4,17(20)-(trans)-pregnediene-3,16-dione, 16β-acetyloxy-pregn-4,17(20)-trans-dien-3-one, 3α-acetyloxy-5α-pregnan-16-one, 20R,22R-dihydroxycholest-4-en-3-one, guggulsterol-I, isocembrol **172**, 4-epiisocembrol **173**, mukulol, and diayangambin **174**. The 50% aqueous methanolic extract showed potent anti-inflammatory effect on adjuvant-induced air-pouch granuloma in mice[90].



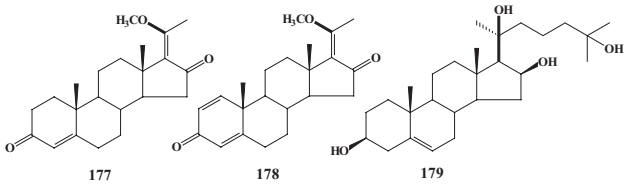


The conformation of steroid nucleus of guggulsterone E **118**, isolated from ethyl acetate extract of *Commiphora mukul*, was studied[91]. The study did not establish the absolute configuration of this molecule. It has been marked in India as hypolipidaemic drug.

Commiphora wightii is a branched shrub or a small tree found in some states of India and Pakistan. Guggul, the exudates of *C. wightii* is used in Ayurvedic literature as medicine. Guggul lipid (= a mixture of lipid steroids isolated from the resin) is a potent hypolipidemic agent. It was found that the ethyl acetate extract of *C. wightii* showed significant in vitro cytotoxicity. After column chromatography two ferrulates were characterized. The absolute configuration of one of the known ferulates (guggultetrol-18 **142**), was deduced as D-*xylo* (2S, 3S, 4R-configuration). The alcohols obtained by hydrolysis of the ferulates were concluded to be a mixture of (Z)-5-tricosene-1,2,3,4-tetraol **175** and (Z)-5-tetracosene-1,2,3,4-tetraol **176** (ref.[92]). This new class of naturally occurring lipids showed strong cytotoxic activity and some free radical scavenging activity.

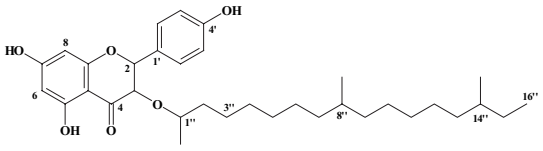


Three new and five known compounds were isolated from the oleogum resin of *Commiphora wightii* (Arnott.) Bhand. [syn. = *Commiphora mukul* (Hook ex Stocks) Engl.], which is endemic to the Indian peninsula and grows wild in India and Pakistan. This exudates possess a variety of pharmacological activities. Five previously isolated compounds were Z-guggulsterone **117**, E-guggulsterone **118**, guggulsterol-I **119**, myrrhanol A **163** and myrrhanone A **165**. Another three compounds, Guggulsterone-M **177**, dehydroguggulsterone-M **178** and guggulsterol-Y **179**, were new[93].



177 178 179

An ethanolic extract of air-dried trunk of *Commiphora wightii* (Arn.) Bhandari (= *C. mukul* Hoox ex Stocks) was separated on column packed with silica gel to give a new antifungal flavone named muscanone **180** and already known naringenin 181 (ref.[94]). Muscanone was active agains *Candida albicans* in microbial sensitive assay.



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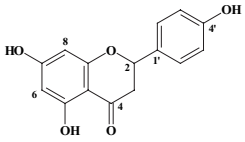
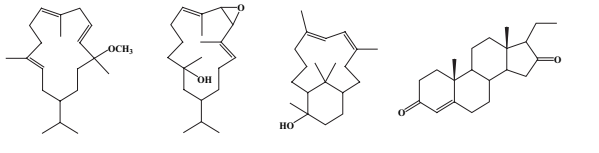
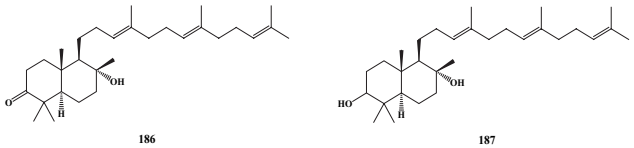


181

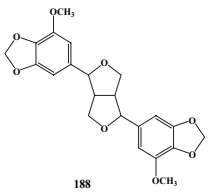
Guggulu, the gum resin from Commiphora mukul, was boiled with water prior to extractions. Bioassay-guided isolation of compounds from the hexane-soluble portion of the methanol extract of guggulu yielded 14 compounds. Seven of them, (1E,4E,8E)-4,8,14-trimethyl-11-(1-methylethyl)-14-methoxycyclotetradeca-1,4,8-triene **182**, (2E,12E)-2,7,13-trimethyl-9-(1-methylethyl)-15-oxabicyclo[12.1.0]pentadeca-2,12-dien-7-ol **183**, (4Z,6E)-4,7,12,15,15-pentamethylbicyclo[9.3.1]pentadeca-4,6-dien-12-ol **184**, pregn-4-ene-3,16-dione **185**, (13E,17E,21E)-8-hydroxypolypodo-13,17,21-trien-3-one **186**, (13E,17E,21E)-polypodo-13,17,21-triene-3,18-diol **187** and 5,5'-tetrahydro-1H,3H-furo[3,4-c]furan-1,4-diylbis[7-(methoxy)-1,3-benzodioxole] **188** were novel compounds[95].



182 183 184 185



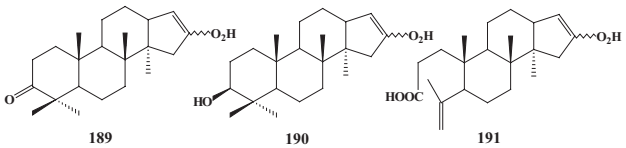
186 187



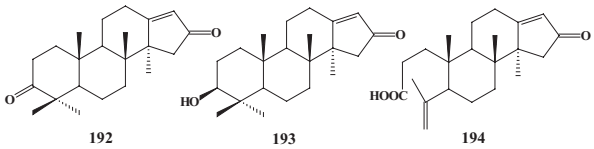
188

Other *Commiphoras*

During the initial study were found in petrol extract of the stem bark of *Commiphora kua* three labile C_{22} octanordammarane triterpenes, 16-hydroperoxymansumbin-13(17)-en-3-one **189**, 16-hydroperoxymansumbin-13(17)-en-3β-ol **190** and 16-hydroperoxy-3,4-*seco*-mansumbin-3(28),13(17)-dien-3-oic acid **191** which rapidly degraded to give breakdown products identified as mansumbin-13(17)-en-3,16-dione **192**, 3β-hydroxymansumbin-13(17)-en-16-one **193** and 16-oxo-mansumbin-3(28),13(17)-dien-3-oic acid **194** (ref.[96]).

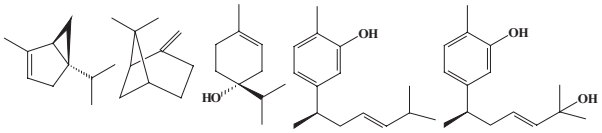


189 190 191



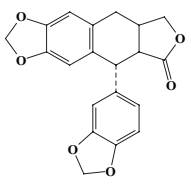
192 193 194

Steam distillation of the oleo-resin of *Commiphora kua* var. *kua* Vollesen (syn. *Commiphora flaviflora*), a tree growing wild in Kenya, Ethiopia and Somalia, gave a volatile oil, in which was found α-pinene **1**, p-cymene **45**, α-thujene **195**, β-pinene **196**, limonene **2**, sabinene **96**, terpinene-4-ol **197**, car-3-ene **97** and myrcene **52**. In the residue after steam distillation and after ethyl acetate extraction and column chromatography were identified these known furanosesquiterpenoids, 2-O-acetyl-8,12-epoxygermacra-1(10),4,7,11-tetraene **24** and 2-O-methyl-8,12-epoxygermacra-1(10),4,7,11-tetraene **25**, a known bisabolene, xanthorrhizol **198**, and a new bisabolene, 2-methyl-5-(5'-hydroxy-1',5'-dimethyl-3'-hexenyl)phenol **199** (ref.[97]).



195 196 197 198 199

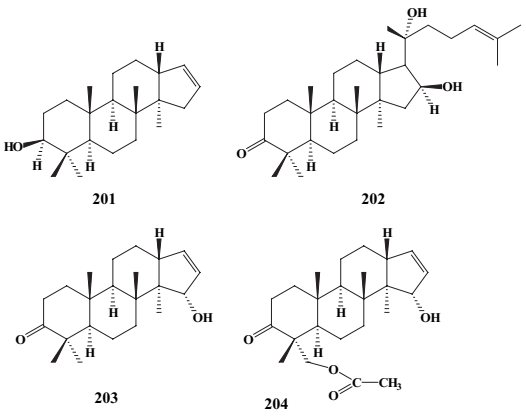
Four active compounds, mansumbinone **146**, mansumbinoic acid **147**, picropolygamain **200** and lignan-1 (methoxy-1,2,3,4-tetrahydropolygamain) have been purified from anti-inflammatory extracts of *Commiphora kua*[98]. These molecules inhibit the formation of myeloperoxidase products.



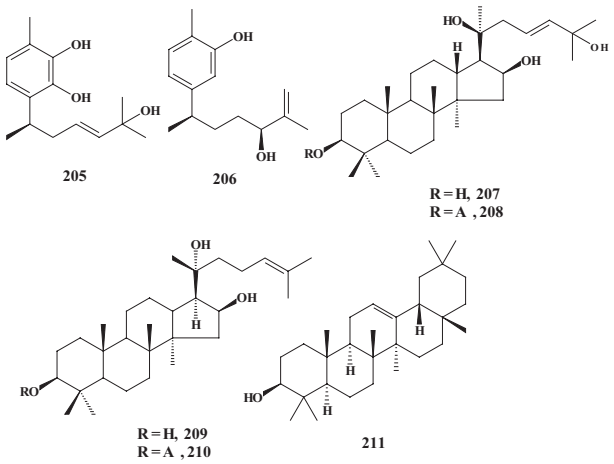
200

Commiphora kua (J. F. Royle) Voleesen var. *gowlello* (Sprague) J. B. Gillett, a 3-5 m tall tree is found mainly in Kenya, Somalia, Ethiopia and Arabia. It produces wood that is used to make household utensils, furniture and tools. During rainy season, its trunk is cut and sucked to quench thirst. In dry season, the tree produces a brown resin, which is used as incense.

Ground resin from this tree was extracted with petrol. TLC analysis of this extract indicated the presence of at least six compounds. With the help of column chromatography over silica gel four already known compound – mansumbinone **146**, mansumbinol **201**, (16S, 20R)-dihydroxydammar-24-en-3-one **202** and T-cadinol **70** – and two new octanordammarane triterpenes, 15α-hydroxymansumbinone **203** and 28-acetoxy-15α-hydroxymansumbinone **204**, were isolated and identified. Structures of these two compounds were elucidated by spectroscopic techniques (MS, IR, UV, ^{1}H- and ^{13}C-NMR, X-ray analysis)[99].

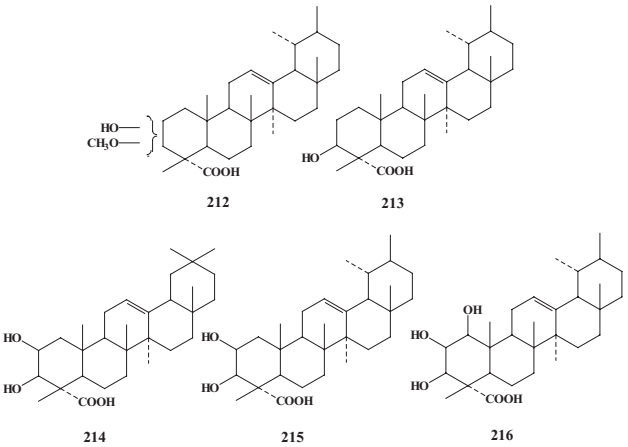


The residue from steam distilled resin of *Commiphora kua*, collected near Wajir in Kenya, a novel bisabolene, 6-hydroxy-2-methyl-5-(5'-hydroxy-1'(R),5'-dimethylhex-3'-enyl)-phenol **205** together with two new dammarane triterpenes, 3β,16β,20(S),25-tetrahydroxydammar-23-ene **207** and 3β-acetoxy-16β,20(S),25-trihydroxydammar-23-ene **208**, have been isolated after extraction with ethyl acetate and column chromatography on silica gel. In addition were identified known compounds as 2-methyl-5-(4'(S)-hydroxy 1'(R),5'-dimethylhex-5'-enyl)-phenol **206**, 3β,16β,20(R)-trihydroxydammar-24-ene **209** and its acetate derivative, 3β-acetoxy-16β,20(R)-dihydroxydammar-24-ene **210**, β-amyrin **211** and its acetate derivative, 2-methoxyfuranodienone, and 2-acetoxyfuranodienone. 2-Methyl-5-(4'(S)-hydroxy-1'(R),5'-dimethylhex-5'-enyl)-phenol **206** displayed fungicidal activity against *Cladosporium cucumernum* on TLC assay[100].



The genus *Commiphora* Jacq. (= *Balsamodendron* Kunth), natural order Burseraceae, has not been extensively studied before. Myrrh is usually obtained from *C. abyssinica* (Berg) Engl., *C. molmol* Engl. and *C. opobalsamum* (L.). It has been found to consist of volatile oils, mostly mono- and sesquiterpenes. The presence of triterpenes has never been suggested.

C. pyracanthoides Engl. (= *C. glandulosa* Schinz), a tree growing in the arid parts of Southern Africa, is rich source of triterpene acids, both free and combined as glycosides. Five free acids (comic acid A **212**, B **213**, C **214**, D **215**, and E **216**) were isolated from the ethereal solution of the resin[101]. In contrast, the resin from *C. mukul* is completey devoid of triterpenoids.



The structures of commic acid C (2β,3β-dihydroxy-olean-12-ene-23-oic acid) **214** and commic acid D (2β,3β-dihydroxyurs-12-ene-23-oic acid) **215** with two hydroxyl groups and one double bond from *Commiphora pyracanthoides* Engl. were elucidated[102].

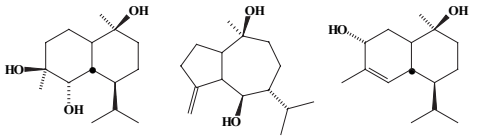
Another communication concerns the structure of comic acid E **216** (1β,2β,3β-trihydroxyurs-12-ene-23-oic acid) with three hydroxyl groups from *Commiphora pyracanthoides* Engl.[103].

From the essential oil of *C. guidotti*, isolated by steam distillation of the gum resin, seven sesquiterpene hydrocarbons and one furanosesquiterpenoid, fuaranodiene,

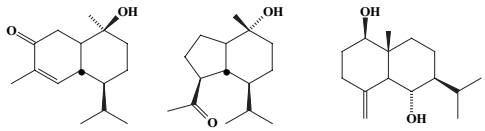
were identified. The GC/MS revealed car-3-ene **97**, α- **84** and β-santalene **88**, epi-β-santalene **87**, β-bergamotene **85**, β-farnesene **89**, α- **99** and β-bisabolene **47**, and furanodiene 36 (ref.[104]). The structures of three main compounds – α-santalene, α-bisabolene and furanodiene – were confirmed, after their isolation with the help of HPLC in pure form, by MS, ^{1}H-NMR and ^{13}C-NMR.

An ethyl acetate extract of a resin of *Commiphora guidottii* Chiov. (scented myrrh, bissabol) gave after purification on column packed with silica gel the pharmacologically active (smooth muscle relaxing effect) sesquiterpene (+)-T-cadinol **69** (ref.[105]).

Ethyl acetate extract of scented myrrh (*Commiphora guidotti* Chiov.) was purified by silica gel chromatography and seven compounds were obtained. The major component, T-cadinol **69**, has previously been shown to possess smooth muscle-relaxing properties. Between other isolated compounds, more polar sesquiterpenes, cadinanetriol (4β,5α,10β-trihydroxycadinane) **217** and guaiane (6β,10β-dihydroxy-4(15)-guaiene) **218** were new compounds. 3α-Hydroxy-T-cadinol **219** and 3-oxo-T-cadinol **220** were reported for the first time as natural products. Already known isolated compounds were identified as (-)-oplopanone **221** and eudesme 222 (ref.[106]). The smooth muscle relaxing properties of all isolated compounds were 5–10 times less potent than that of T-cadinol (cadinanetriol was inactive).



217 **218** **219**



220 **221** **222**

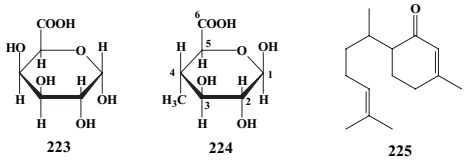
It is concluded that the botanical origin of scented myrrh – "bissa bol" (Hindi) or "hebbakhade" (Somali) – a major article for export from Somalia since ancient times, is *Commiphora guidottii* (Burseracae) and not *C. erythraea* as generally has been presumed. The reasons for the previous confusion were discussed and an updated synonymy and distribution map for C. guidottii was given[107].

The mass spectra of previously isolated methyl commates A to E **212–216** from *Commiphora pyracanthoides* were illustrated[108].

From hexane extract of the essential oil of *Commiphora abyssinica* (Berg) Engler have been with the help of column and preparative chromatography isolated α-pinene **1**, limonene **2**, dipenthene, cuminaldehyde **3**, cinnamaldehyde **4**, eugenol **5**, *m*-cresol **6**, formic acid, acetic acid, palmitic acid, nine sesquiterpene hydrocarbons (δ-elemene **41**, β-elemene **39**, α-copaene **53**, β-bourbonene **44**, germacrene D **60**, caryophyllene **56**, humulene **57**, γ-cadinene **64** and δ-cadinene **65**), the sesquiterpene alcohol (elemol **42**) and the furanosesquiterpenoids furanodiene **36**, furanodienone **18**, isofuranogermacrene **13**, curzerenone **17** and lindestrene **16** (ref.[109]).

A Bursera latex containing 6.5% steroid fraction (a) was obtained from *Commiphora abyssinica* and separated by column chromatography to give a, m. 144-6°, $[\alpha]_D^{20}$ –37°, and a was acetylated to give a product, mp. 112°, $[\alpha]_D^{20}$ –45°. The mass spectrum of a shows the presence of cholest-5-en-3β-ol **116** (b), $[\alpha]_D^{20}$-39°, Δ^5-campestan-3β-ol **136** (c), $[\alpha]_D^{20}$-33°, and Δ^5-sitostan-3β-ol **112** (d), $[\alpha]_D^{20}$ -36°. NMR data for a were given. a contains 68 % b, 9 % c, and 5 % d (ref.[110]).

The gum of Bdellium that was studied was African in origin, produced by *Commiphora africana*. The Galbanum gum probably came from *Ferula galbaniflua*. The former gum was more resistant to hydrolysis than the latter, contained more protein, and consumed more periodate during oxidation. In both instances galactose **27** and arabinose **28** were resistant to oxidation, suggesting that these sugars were involved in 1→3 linkages or branching at position 3. The amount of HCOOH produced was higher in the case of Bdellium gum, and suggested the oxidation of terminal molecules and branching. The uronic acids were galacturonic **220** and 4-methyl-glucuronic **224**, the latter predominating[111].



223 **224** **225**

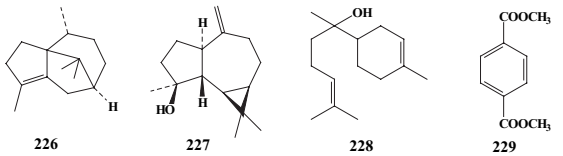
The essential oils obtained from the leaves of *Commiphora africana* and *Xylopia aethiopica* from Benin were analyzed by GC, GC/MS and ^{13}C-NMR. Leaf essential oil of *C. africana* contained fairly high amounts of sesquiterpenes, among which α-oxobisabolene **225** was the most important (61.6 %). *X. aethiopica* was characterized by a high content of β-pinene **196** (34.9 %), elemol **42** (14.9 %) and α-pinene **1** (11.6 %)[112]. The leaf essential oil of *X. aethiopica* contained mainly sesquiterpenoid compounds which amount to about 36.6 %.

The leaf oil of *Commiphora africana*, obtained by hydrodistillation, has been analyzed by GC, GC/MS coupling and ^{13}C-NMR spectroscopy (Table 5). The two major compounds identified in the oil were α-oxobisabolene **225** (61.6 %) and γ-bisabolene **100** (10.0 %)[113].

The methanolic extract of bark of the plant *Commiphora africana* gave a homogenous product through chromatographic separation which after crystallization from methanol furnished needles characterized as dimethylterephthalene (benzene-1-dicarboxylic acid dimethylester) **229** on the basis of spectral analysis[114].

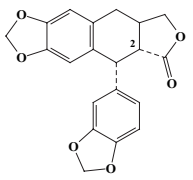
Table 5. Relative concentrations (%) of volatile components of the leaf oil of *Commiphora africana* (A. Rich.) Engl. from Benin.

Compound	Percentage
α-thujene **195**	0.1
α-pinene **1**	0.2
p-cymene **45**	0.1
1,8-cineole **152**	0.1
cyperene **226**	0.4
β-caryophyllene **56**	0.4
(Z)-β-farnesene **89**	4.7
aromadendrene **58**	1.5
α-humulene **57**	0.2
ar-curcumene **101**	3.5
germacrene D **60**	0.5
β-selinene **38**	0.4
β-bisabolene **47**	3.1
(Z)-γ-bisabolene **100**	10.0
spathulenol **227**	0.2
α-bisabolol **228**	4.0
α-oxobisabolene **225**	61.6
ar-curcumene **101**	3.5



226 227 228 229

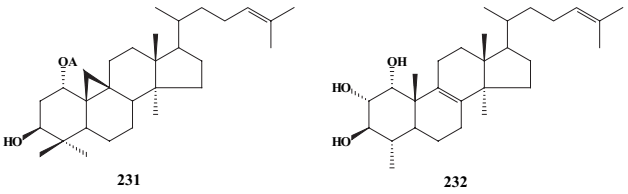
A heavily spined shrub or small tree found in Kenya, *Commiphora incisa* Chiov. (syn. *C. candidula* Sprague), exudes after injury a liguid, which quickly hardens and formed resin becomes with age crystalline. An ether extract of this resin was prepared. On chromatographic column packed with silica two aryltetralin lignans were isolated. The first lignan appeared to be the known lignan polygamain **230** [Hokanson G.C.: J. Nat. Prod. 42, 378 (1979)] previously reported from *Polygala polygama* Walt. The second one, an isomer of the first one, was identified as picropolygamain **200** (ref.[115]).



230

The resin of *Commiphora incisa* Choiv. (syn *C. candidula* Sprague) collected in Kenya and extracted with diethyl ether gave after purification on column with silica gel two already known lignans (polygamain and picropolygamain) and four triterpene deraivatives (mansumbinone **146**, 3,4-*seco*-mansumbinoic acid **147**, mansumbinol **201** and 16(S),20(R)-dihydroxydammar-24-en-3-one) **202** (ref.[116]). (It was later found to be *C. kua*.)

Authors referred, that about one half of the samples, previously reported as *Commiphora incisa* has now been identified as being of *Commiphora kua* (J. F. Royle) Vollesen (?syn. *C. flaviflora*). Diethyl ether extracts of *C. incisa* gave after chromatographic column minor compound 1α-acetoxy-9,19-cyclolanost-24-en-3β-ol **231** and the major compound 29-norlanost-8,24-dien-1α,2α,3β-triol **232** (ref.[117]).

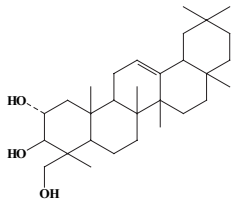


231 232

Commiphora rostrata grows in Kenya, Somalia and Ethiopia. It is small tree up to 3 m height. The simple leaves are edible. Gas chromatography revealed in the oil from stem bark volatile resin at least 30 components, the 22 have been identified as: 2-octanone, 2-nonanone, 2-decanone (65 % in resin), 2-undecanone (24 %), 2-dodecanone (5 %), 2-tridecanone, 3-undecanone, 2-tetradecanone, 2-pentadecanone, 2-decanol, 2-undecanol, 2-dodecanol, 2,2-dimethylnonanol, 2,2-dimethyldecanol, 2,2-dimethylundecanol, 2,2-dimethyldodecanol, tridecanal, tetradecanal, pentadecanal, hexadecanal (1.5 %), heptadecanal and octadecanal[118]. It seems probable that the volatile resin of *C. rostrata* plays a role in defence against potential pests and pathogens.

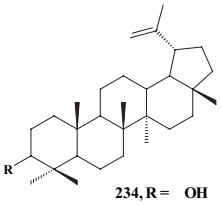
The major alkanone constituents of the resin of *Commiphora rostrata*, 2-decanone and 2-undecanone, and a series of structural analogues were bioassayed for their repellency against the maize weevil, *Sitophilus zeamais* in olfactometric assays[119]. All the aliphatic ketones and aldehydes showed comparable or greater activity than the synthetic commercial insect repellent *N,N*-diethyl toluamide (DEET). In the 2-alkanone series the C-8 and C-9 compounds demonstrated significantly higher activity than their shorter- and longer-chained congeners. Analogues differing in the relative positions of the carbonyl group, including aldehydes, showed a variable pattern of repellency. Alkanols appeared to be mildly attractive to the weevil. The results supported author's previous suggestion that the resin constituents may play an allomonal role in the ecosystem where the plant thrives.

A new pentacyclic triterpene, 2α,3β,23-trihydroxyolean-12-ene **233**, was isolated from the roots of *Commiphora* merkeri[120]. The compound has anti-inflammatory and analgesic activity.

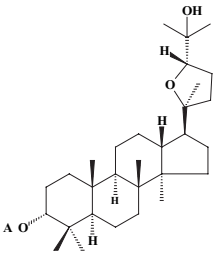


233

Extraction of the stem bark of *Commiphora dalzielli* Hutch. (a shrub or small tree indigenous to Ghana) with petroleum gave seven dammarane triterpenes. The two compounds were identified as common lupeol **234** and β-amyrin **211**. Five of them were separated by column chromatography with silica gel and circular preparative thin-layer chromatography. After purification epilupeol **235**, cabraleadiol 3-acetate **236**, cabraleone **237**, cabraleadiol **238** and isofouquierone 239 (ref.[121]). Both the acetate and isofouquierone appear to be new compounds.



234, R = OH
235, R = αOH



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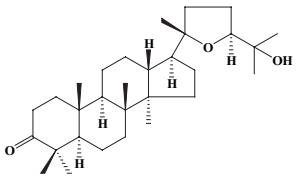

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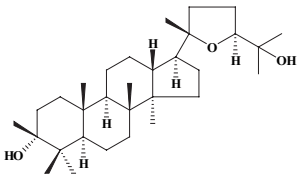

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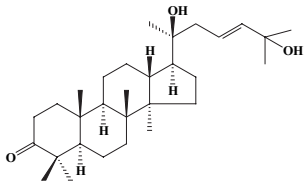


239

In the essential oil of *Commiphora quadricincta* a large number of the compounds were identified by GC-MS and the following compounds with retention times of authentic samples (Table 6). A significant number of the compounds identified were terpenoids. Volatiles collected before the rains were comparatively richer, particularly in the more volatile fractions[122].

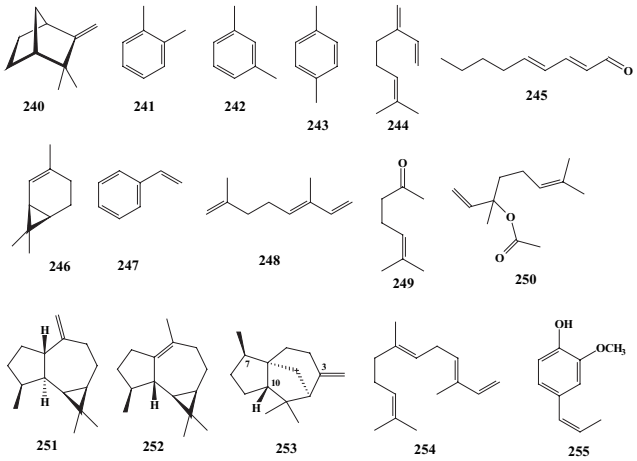
Table 6. Compounds identified in the essential oil of *C. quadricincta* (evidence by MS and retention time).

Compound	Before rains	After rains
α-pinene **1**	+	–
camphene **240**	+	–
β-pinene **196**	+	+
o-xylene **241**	–	+
m-xylene **242**	+	+
p-xylene **243**	–	+
β-myrcene **244**	+	–
limonene **2**	+	+
α-phellandrene **148**	+	–
(E,E)2,4-nonadienal **245**	+	+
β-ocimene **26**	+	+
4-carene **246**	+	–
styrene **247**	–	+
phenylacetaldehyde	–	+
α-ocimene **248**	–	+
p-cymene **45**	+	+
α-terpinolene **96**	+	+
4-nonanone	+	–
6-methyl-5-hepten-2-one **249**	+	+
3,4-dimethyl-octane	+	–
1-hexanol	–	+
nonanal	+	–
1-heptanol	–	+
α-cubebene **43**	+	+
linalool **153**	+	+
copaene **53**	+	+
(Z)-β-farnesene **89**	+	+
linalyl acetate **250**	–	+
caryophyllene **56**	+	+
(+)-aromadendrene **251**	+	+
alloaromadendrene **58**	+	+
(E)-β-farnesene **89**	+	+
ledene **252**	–	+
γ-cadinene **64**	+	+
β-cedrene **253**	+	–
α-farnesene **254**	–	+
α-guaiene **63**	+	+
(E)-isoeugenol **255**	+	–

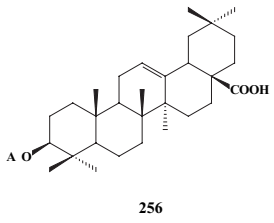
Table 7. Composition of the essential oil in the oleo-resin of *Commiphora tenuis*.

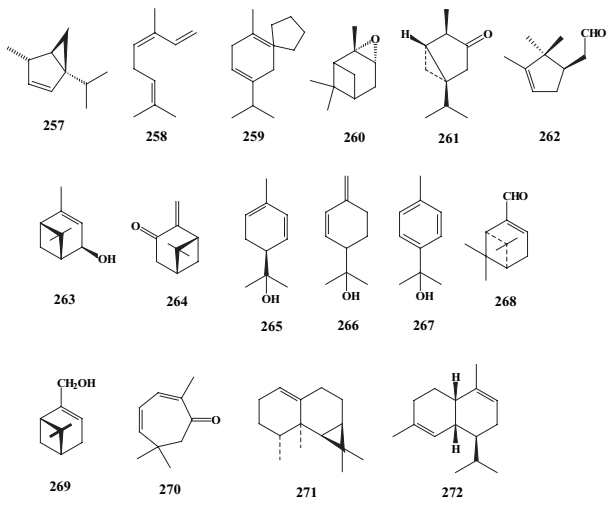
Compound	Area %
α-thujene **195**	8.94
α-pinene **1**	60.84
camphene **240**	0.26
sabinene **96**	6.29
β-pinene **196**	8.79
β-myrcene **61**	1.80
3-carene **97**	3.66
p-cymene **45**	0.90
β-thujene **257**	0.91
limonene **2**	5.52
cis-β-ocimene **258**	0.15
trans-β-ocimene **26**	< 0.1
γ-terpinene **259**	tr
α-pinene-epoxide **260**	tr
α-thujone **261**	tr
α-campholenal **262**	tr
trans-verbenol **263**	tr
verbenol **263**	tr
pinocarvone **264**	tr
p-mentha-1,5-dien-8-ol* **265**	tr
p-mentha-1(7)-dien-8-ol* **266**	tr
terpinen-4-ol **197**	tr
p-cymen-8-ol **267**	tr
myrtenal **268**	tr
α-terpineol **46**	tr
myrtenol **269**	tr
bornyl acetate **151**	tr
eucarvone **270**	tr
copaene **53**	0.26
β-bourbonene **44**	tr
β-elemene **39**	1.07
β-caryophyllene **56**	< 0.1
humulene derivative	tr
alloaromadendrene **58**	tr
β-gurjunene **271**	tr
β-selinene **38**	tr
α-selinene **62**	tr
α-muurolene **272**	tr
δ-cadinene **65**	tr

* = tentative identification



An exudate from *Commiphora tenuis* was collected in Ethiopia. After removal of the gum from the gum-resin and column chromatography four free triterpenes. The main triterpene was characterized as 3β-O-acetoxyolean-12-en-28-oic acid **256** (ref.[123]). After steam distillation the oil was taken up in n-pentane and analyzed by GC and GC-MS. Composition of the essential oil in the oleo-resin was as follows (37 compounds were identified – Table 7).



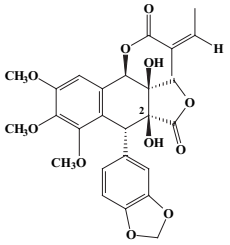


It was shown that several compounds which were previously reported to occur in myrrh are not present in true myrrh but originate from adulterant resins of other *Commiphora* species. This is also the case of 2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one with

stereochemistry as (1(10)E,2R*,4R*)-2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one **22** and furanodienone with stereochemistry as (1(10)E,4E)-8,12-epoxygermacra-1(10),4,7,11-tetraen-6-one **18** (ref.[124]). These compounds are obtained from the resin of other *Commiphora* species, namely *C. sphaerocarpa*, *C. holtziana* and *C. kataf*. In this work both compounds were isolated from petrol extract of the resin of *C. sphaerocarpa* and analyzed by X-ray crystallography and NMR for stereochemistry (are given ^{13}C-NMR spectral data of furanodiene).

Very little is known about the chemistry of resins derived from others than usually studied *Commiphora* species, of which there are more than 50 in Ethiopia[125].

Commiphora erlangeriana, occurring in Ethiopia and Somalia is known as "dhunkal". "Dhunkal" resin is toxic to humans and animals. However, the fruits are edible and sold in markets during rainy seasons. The powder resin was extracted with a mixture of methanol – ethyl acetate. After column chromatography four new lignans were identified in extract, two of the polygamain-type, named erlangerin A **273** (the most abundant compound – 41 %) and erlangerin B **274**, and two related to podophyllotoxin, named erlangerin C **275** and erlangerin D **276** (ref.[126]).



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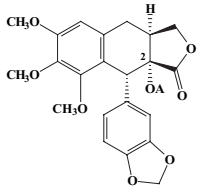

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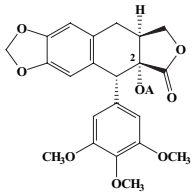

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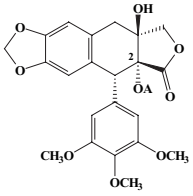
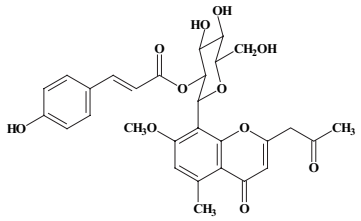


276

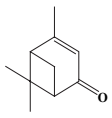
As the resin of *Commiphora erlangeriana* is known to be poisonous to humans and animals and has traditionally been used as an arrow poison, the recently found four erlangerins (A to D) were studied for their toxicity to mammalian cells. Two human (HeLa and EAhy926) and two murine (L929 and RAW 264.7) cell lines were used for toxicity assays. As assessed by the MTT assay, the effects of erlangerin C and D closely follow the activity profile of podophyllotoxin: they induced a concentration-dependent cytotoxicity in the murine macrophage cells (RAW 264.7) and a cytostatic effect in HeLa, EAhy926 and L929 cells. In contrast, erlangerins A and B suppressed cell viability at relatively higher concentrations (EC_{50} values higher than 3μM as compared with nM concentration range for erlangerins C and D and podophyllotoxin) and their activity appears to be consistent with a cytotoxic mode of action in all cell lines studied[127].

A new 5-methylchromone glycoside, named 7-O-methylaloeresin A (2-acetonyl-8-C-β-D[2'-O-(E)-4-hydroxycinna moyl]glucopyranosyl-7-methoxy-5-methylchromone) **277**, was isolated from *Commiphora socotrana* (Burseraceae)[128]. Its structure was elucidated by spectroscopic data (MS, UV, ^{1}H- and ^{13}C-NMR).



277

Volatile oils obtained by the steam distillation of aromatic resin with attractive odour from *Boswellia neglecta*, *Commiphora africana*, *Commiphora campestris* and *Commiphora ogadensis* have been examined by capillary GC and GC/MS. In each case the volatile oils appeared entirely monoterpenoid in constitution (Table 8). All four oils were generally characterized by high concentration of α-pinene **1**. Other constituents that were important markers of individual species included α-thujene **195** (*B. n.*, *C. a.*), sabinene **96** (*C. c.*), myrcene **52**, car-3-ene **97** (*C. o.*) and p-cymene **45** (*B. n.*, *C. a.*)[129].



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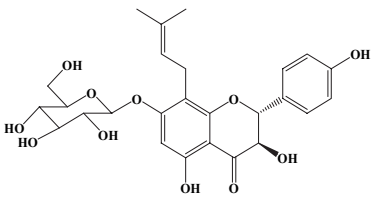
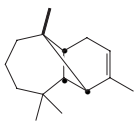


279

Bioassay-guided fractionation of a crude extract from *Commiphora africana* led to the isolation of the dihydroflavonol glucoside phellamurin **279** (ref.[130]).



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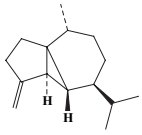


281

Samples of the liquid resin obtained spontaneously on cutting the woody parts of *Commiphora terebinthina Vollesen* (which occurs widely in northern Kenya and southern Ethiopia) and *Commiphora cyclophylla* Chiov. (occurs in southern Ethiopia) were examined. Both consist primarily of monoterpene hydrocarbons (no oxygenated derivatives were detected) with limonene **2** as the major component; the resin from *C. t.* was richer in sesquiterpenes (Table 9)[131].

Table 8. Concentration (%) ranges of 12 monoterpenes in the volatile portion of the resins.

Terpene	*C. africana*	*C. campestris*	*C. ogadensis*
α-thujene **195**	3.9–42.4	–	0–1.3
α-pinene **1**	23.8–67.2	32.6–83.0	37.1–68.8
camphene **240**	0–2.4	0–3.1	–
sabinene **96**	0–10.4	1.0–37.3	0 – 1.0
β-pinene **196**	4.2–12.1	2.8–9.7	1.1–2.3
myrcene **52**	0–2.1	–	3.0–38.6
α-phellandrene **150**	–*	–	–
car-3-ene **97**	0–1.7	–	8.6–16.8
p-cymene **45**	0–28.0	0–3.3	–
limonene **2**	0–8.6	0–.8	2.6–2.7
terpinen-4-ol **197**	0–13.1	0–14.4	–
verbenone **278**	0–7.1	0–3.0	–

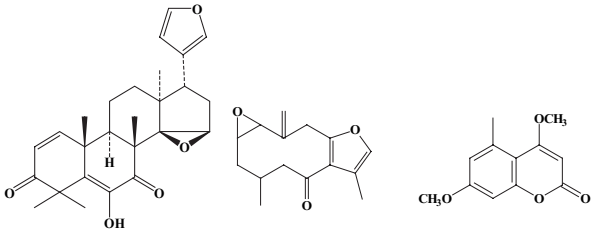
* Present in two West African samples from Bourkina Faso

Table 9. Relative concentrations (%) of volatile components of the resins.

Compound	*C. terebinthina*	*C. cyclophylla*
α-thujene **195**	–	11.9
α-pinene **1**	5.7	12.0
sabinene **96**	4.7	12.1
β-pinene **196**	0.6	1.9
myrcene **52**	1.4	2.0
decane	0.5	–
car-3-ene **97**	0.5	1.8
limonene **2**	50.4	46.9
δ-elemene **41**	0.2	–
longipinene **280**	0.8	–
α-cubebene **43**	3.9	–
β-elemene **39**	3.0	0.7
t-caryophyllene **56**	1.4	0.1
β-cubebene **281**	11.1	0.2
α-muurolene **272**	3.7	–
δ-cadinene **65**	1.6	–

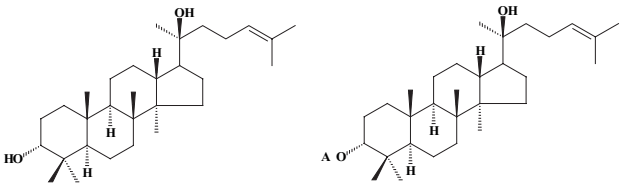
The resins from the African Burseraceae are important items of commerce, as glues, tick repellents, medicinals and perfumes. The content compounds of these resins are not yet well identified. Three known - (1E)-3-methoxy-8,12-epoxygermacra-1,7,10,11-tetraen-6-one **35**, *rel*-2R-methyl-5S-acetoxy-4R-furanogermacr-1(10)Z-en-6-one **34** and (1(10)E,2R*,4R*)-2-methoxy-8,12-epoxygermacra-1(10),7,11-trien-6-one **22** - and one novel furanogermacrenes have been isolated and identified from the ethanolic extract of a resinous exudates (a commercial sample) of *Commiphora holtziana* from Kenya. The structure of the known compounds was determinated by comparison of ^{1}H- and ^{13}C-NMR spectra with those already published. The structure of the novel compound was determined as 1,2-epoxyfurano-10(15)-germacren-6-one **283**, using spectrometric techniques. Some previous ^{13}C-NMR assignments for the known compounds were corrected or clarified[132].

β-sitosterol **112**, m.p. 138°, and cedrelone **282**, m.p. 203-4°, were isolated from hexane extracts of *Balsamodendron pubescens* roots as well as a 4,7-dimethoxy-5-methylcoumarin characterized as siderin **284** (ref.[133]). A novel synthesis of siderin and 6,8-dimethoxy-4-methylcoumarin was given.

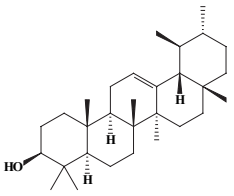


282 **283** **284**

The resin of *Commiphora confusa* afforded two new dammarane triterpenes, (3*R*,20*S*)-3,20-dihydroxydammar-24-ene **285** and (3*R*,20*S*)-3-acetoxy-20-hydroxydammar-24-ene **286** along with the known triterpenes, cabraleadiol 3-acetate **236** and α-amyrin **287** (ref.[134]).

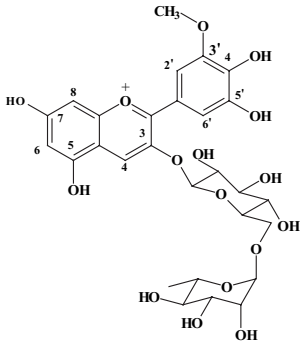


285 **286**



287

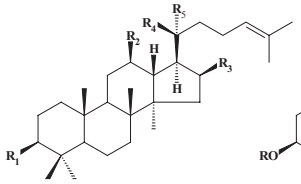
Color and precipitation reactions proved the presence of condensed tannins and these were detected for the powdered bark and alcoholic extract of *Commiphora angolensis*, respectively. An unsuccessful attempt was made by using ascending paper chromatography to identify the phenolic compounds present. By elution of a fraction separated on a thick paper chromatogram with HCl-MeOH, ascending paper chromatography separated petunidin 3-rhamnoglucoside **288** (buthanol - acetic acid - water, BuOH - HCl and 1% HCl)[135].

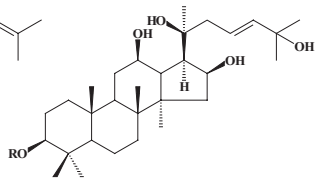


288

Seeds of *Commiphora guillaumini* Perr. tree were collected at Madagascar. The frozen arils were ground and extracted with cyclohexane. Supercritical fluid chromatography – atmospheric pressure chemical ionization mass spectrometry was employed for the determination of the lipid composition in the arils. From tri- and diacylglycerols tripalmitoylglycerol (PPP), PPS, PPO, PPL, POS, POO, PLO, LSS, POLn, OSS, OOS, OOO, OOL, OLL, LLL, OP and OO (P = palmitoyl, S = stearoyl, O = oleoyl, L = linoleoyl, Ln = linolenoyl) were identified. From identified triacylglycerols and diacylglycerols are possible all positional permutations, since it is not possible to determine the positional isomers of the glycerols by MS. The assigned structure represents one of the possible positional permutations. The presence of the known ant attractant 1,2-dioleoylglycerol in arils of the seeds of *C. guillaumini* was confirmed[136].

The steam distilled resin residue of *Commiphora confuse* samples obtained from well identified trees (around Saltlik, Kenya) has yielded after acetone extraction and following column chromatography on silicagel four novel dammarane triterpenes characterised as (20S)-3β-acetoxy-12β,16β-trihydroxydammar-24-ene **289**, (20S)12β,16β-trihydroxydammar-24-ene-3β-O-β-glucopyranoside **290**, (20S)-3β-acetoxy-12β,16β,25-tetrahydroxydammar-23-ene **291**, and (20S)-3β,12β,16β,25-pentahydroxydammar-23-ene **292**. The known compounds β-amyrin **211**, 3β-amyrinacetate, 2-methoxyfuranodienone, 2-acetoxyfuranodienone, (20R)-3β-acetoxy-16β-dihydroxydammar-24-ene **293**, 3β-hydroxydammar-24-ene **294**, 3β-acetoxydammar-24-ene **295**, 3β-acetoxy-16β-hydroxydammar-24-ene **296**, (20R)-3β,16β-trihydroxydammar-24-ene **297**, and β-sitosterol **112** were also isolated from the same extract. The structures of the compounds were determined using spectroscopic, physical, and chemical methods[137].





	R_1	R_2	R_3	R_4	R_5
289	OA	OH	OH	OH	CH_3
290	O-glu	OH	OH	OH	CH_3
291	OA	H	OH	CH_3	OH
292	OH	H	H	H	CH_3
293	OA	H	H	H	CH_3
294	OA	H	OH	H	CH_3
295	OH	H	OH	CH_3	OH

296 R = A
297 R = H

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