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About the Institute
The Hunt Institute for Botanical Documentation, a research division of Carnegie Mellon University, specializes in the history of botany and all aspects of plant science and serves the international scientific community through research and documentation. To this end, the Institute acquires and maintains authoritative collections of books, plant images, manuscripts, portraits and data files, and provides publications and other modes of information service. The Institute meets the reference needs of botanists, biologists, historians, conservationists, librarians, bibliographers and the public at large, especially those concerned with any aspect of the North American flora.

Hunt Institute was dedicated in 1961 as the Rachel McMasters Miller Hunt Botanical Library, an international center for bibliographical research and service in the interests of botany and horticulture, as well as a center for the study of all aspects of the history of the plant sciences. By 1971 the Library's activities had so diversified that the name was changed to Hunt Institute for Botanical Documentation. Growth in collections and research projects led to the establishment of four programmatic departments: Archives, Art, Bibliography and the Library.

→ WARNING: ALTERATION, ADDITION OR MUTILATION OF ENTRIES IS PROHIBITED. ANY UNOFFICIAL CHANGE WILL RENDER THIS PASSPORT INVALID.

NAME - NOM
ROBERT MERRILL KING

BIRTH DATE - DATE DE NAISSANCE
FEB. 13, 1930

BIRTHPLACE - LIEU DE NAISSANCE
MAINE, U.S.A.

HEIGHT - TAILLE
6 FEET PIEDS 3 INCHES POUCES

HAIR - CHEVEUX
BLOND

EYES - YEUX
HAZEL

WIFE / HUSBAND - EPOUSE / EPOUX
X X X

ISSUE DATE - DATE DE DELIVRANCE
JAN. 7, 1976

MINORS - ENFANTS MINEURS
X X X

EXPIRATION DATE
DATE D'EXPIRATION
JAN. 6, 1981

CANCELLED
NEW APPLICATION
12-3-80

Robert Merrill King
SIGNATURE OF BEARER
SIGNATURE DU TITULAIRE

→ IMPORTANT: THIS PASSPORT IS NOT VALID UNTIL SIGNED BY THE BEARER. PERSONS INCLUDED HEREIN MAY NOT USE THIS PASSPORT FOR TRAVEL UNLESS ACCOMPANIED BY THE BEARER.

Robert M. King

U.S. IMMIGRATION
250 WASHINGTON ST.
BOSTON, MASS.
ADMITTED
UNTIL
AUG 22 1977

U.S. IMMIGRATION
250 WASHINGTON ST.
BOSTON, MASS.
ADMITTED
UNTIL
FEB X7 1977

MEMPHIS STATE UNIVERSITY
Memphis, Tennessee 38111

Department of Biology

22 Oct

Dear Bob

I collected more dried material of Chaptalia this past summer that I'd like to get to Bohlmann. Since you have the connection, would you mind relaying it to him from the Smithsonian. I've sent him a note to say that he might expect it to come from you. The Chaptalia stuff will arrive in a small box (sent Library rate) — containing nothing but the leaves & roots

↓

I had a very good collecting trip this time - got a number of Eupatorieae, which I will send on to US when I get the labels done (hopefully by the end of November)

Sincerely,

Greg

THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

The Department of Botany

Box 165
BIG FORK
Mont. 59911

COPY

Dear Vernon

It seems (as perhaps you already know) that R.M. King will be joint author with ~~A~~ Dr. Harold Robinson of Smithsonian. That is, on A paper to be presented at the Reading Mtgs this next summer.

Would you therefore, send him ~~an~~ a formal invitation, much as extended Dr Robinson. I understand the latter will deliver the paper, but Bob does want to attend the Mtgs + the letter should prove helpful. Actually he called me and sounded, no was, irritated that he was not invited at the same time as Harold. My fault! I keep forgetting how other people react differently than I do!

Love always
Billie Lee

MO - FAX

To: DR. ROBERT KING, DEPT. OF BOTANY, Smithsonian Institution
Washington,D.C.

FAX Number: 202- 786-25

Date:

Total Pages In this Transmission, INCLUDING THIS COVER PAGE: 1

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MESSAGE

Dear Bob,

I got the letter you sent to me in Brazil today. I have been in the US at Mo since the last week of Sept. I really dont know what to say about your permit to collect in Brazil. Please call me when you can. As regarding the material of Pseudobrickellia pinifolia, I have just written a letter to one of my students to try to collect the material and send it to you. That is not difficult to do. I still have the $5.00 you gave me to pay for the postage,I think ot will cost more than that, but if IBGE pays for it, I'll return the money to you.

Best wished,

Tarcso

****

From: Tarciso S. Filgueiras (Visitor)
Missouri Botanical Garden
P.O. Box 299
St. Louis, Missouri 63166-0299

FAX Number: (314)577-9596

Telephone: (314)577-9520

THE BOTANICAL REVIEW
Interpreting Botanical Progress
Founded in 1935
THE NEW YORK BOTANICAL GARDEN
New York 58, N. Y., U. S. A.

Mr. R. M. King
University of Michigan
Ann Arbor, Mich.

Dear Mr. King:

I shall be glad to inspect your Pereskia article for possible publication in "The Botanical Review", but must inform you that it would not be printed before the middle of next year.

Very truly yours,
The Botanical Review

ehf.l.

Ed. H. Fulling

Editor and Publisher.

Professor R.M. King

National Museum of National History
Smithsonian Institute
Washington D.C.
U.S.A.

M.Bassam M.Aboul-Nasr

Assiut University
Fac. of Science of Sohag
Department of Botany
EGYPT - SOHAG

Dear Prof.

May I introduce my self to you:

My name is M.Bassam M.Aboul-Nasr. I am working by the mean time as an assistant lecturer in the Department of Botany, Faculty of Science of Sohag, Egypt.

I have ob tained my B.Sc. in I976 from the Department of Botany, Faculty of Science, Assiut University; and the major subject was Botany.

In October, I98I, I have obtained my M.Sc. degree from Assiut University and the title of my thesis was" Studies on Soil Fungi of the Red Sea Shore ".

I am very keen to follow my study for my Ph.D. degree in " Plant Taxonomy " in your Department if this is available.

I will be financially supported by the Egyptian Government during the period of my study.

Thank you in advance for your kin help.

Sincerly yours

Bassam

(M.Bassam M.Aboul-Nasr)

Acanthostyles buniifolius (Hooker & Arnott) R. M. King & H. Robinson, Phytologia 22: 111. 1971.

Acritopappus micropappus (Baker)R.M.King & H. Robinson, Phytologia 38:100. 1977.

Acritopappus morii R. M. King & H. Robinson, Phytologia 45:143. 1980.

Addisonia boliviana Rusby, Desc. So. Amer. Pl. 147. 1920. = Helogyne straminea (A. P. Decandolle) B. L. Robinson.

Addisonia virgata Rusby, Bull. Torrey Bot. Club 20:432. 1893 = Helogyne straminea (A. P. Decandolle) B. L. Robinson.

Adenostemma biflorum Lessing, Syn. Comp. 156. 1832. = Wollastonia biflora (Linnaeus) A. P. Decandolle. Heliantheae

Adenostemma rufescens Sch.-Bip. Zoll. Syst. Verz. Ind. Archip. 120. 1854-1855 = Ignota

Ageratina esmeraldae (Cuatrecasas) R. M. King & H. Robinson, Phytologia 24:90. 1972 = Ageratina rhypodes (B. L. Robinson) R. M. King & H. Robinson.

Caradesia pauciflora Rafin. Nom. Illeg. Provisional New Fl. Amer. 4:80. 1836. = Fleischmannia ?

Conoclinium hirsutissimum Sch.-Bip. ex Baker, nom. nud. Mart. Fl. Bras. 6(2):311.1876. *Eupatorium hirsutissimum* Baker = *Dasycondylus* ?

Conoclinium oligolepis Kunze, Linnaea 20:19. 1847. = *Conoclinium betonicum* A. P. Decandolle ?

Eupatorium clibadioides Baker, Kew Bull. 105. 1895. = Incertae Sedis.

ISTHMUS OF TEHUANTEPEC

ACAYUCAN Sr. Fortunado Delgado
Lista de Correos
Acayucan, Veracruz

Rancho Las Hojitas
6 km. from Acayucan on road to San Andres Tuxtla

SAN ANDRES TUXTLA

Sr. Juan Mayol
Bocanegra, #40
San Andres Tuxtla, Veracruz

Juan, Pedro, Enrique Naviga - guides

DONAJI Sr. Cesar Farjas (lumberman - owns Donaji)
address for mail:
Apt. #40
Matias Romero, Oaxaca

PAR23/12 PARAGUAY COMPOSITAE 23 DEC 85

G. Schmeda Hirschmann

677	Stevia amambayensis B.L.Robinson
678	Mikania micrantha H.B.K. dupl.
679	Bidens cynapiifolia H.B.K. dupl.
680	Calea rupicola Chod. dupl.
681	Chromolaena odorata (L.)K&R
682	Angelphytum pseudosilphioides (Hassl.)H.Robins. dupl.
683	Austroeupatorium laete-virens (H.& A.) K&R
684	Chromolaena laevigata (Lam.)K&R
710	Stevia aristata D.Don
711	Aspilia pascalioides Griseb.
712	Spilanthes grisea (Chod.)Moore
713	Vernonia remotiflora L.C.Rich
714	Chromolaena ivaefolia (L.)K&R
716	Gamochaeta pensylvanica (Willd.)Cabrera
719	Angelphytum
717	Spilanthes
720	Tagetes minuta L.
721	Chromolaena ivaefolia (L.)K&R
722	Flaveria bidentis (L.)O.Kuntze
723	Stevia aristata D.Don
724	Stevia aristata D.Don
725	Senecio grisebachii Baker
726	Vernonia itapensis Chod. ?
727	Vernonia brasiliana (L.)Druce
729	Aspilia silphioides (H.& A.) Benth.
729	Aspilia silphioides (H.& A.) Benth. Dup.
731	Pluchea sagittalis (Lam.)Cabrera
733	Wedelia brachycarpa Baker
736	Senecio grisebachii Baker
737	Senecio grisebachii Baker
738	Senecio grisebachii Baker
739	Senecio grisebachii Baker

REPUBLIC OF ARGENTINA

9320 Helianthus annuus L.

9325 Gaillardia megapotamica (Spreng.) Baker var scabiosoides (Arn.) Baker

9326 Hyalis argentea Don

9327 Senecio subulatus Don ex Hook. & Arn.

9333 Baccharis gilliesii A. Gray

9335 Centaurea calcitrapa L.

9336 Chuguiraga erinacea Don

9339 Baccharis pingraea DC.

9340 Hysterionica jasionoides Willd.

9342 Baccharis ulicina Hook. & Arn.

9343 Senecio subulatus Don ex Hook. & Arn.

9344 Baccharis salicifolia (R.&P.) Pers.

9345 Gaillardia megapotamica (Spreng.) Baker var. scabiosoides (Arn.) Baker

9346 Gutierrezia gilliesii Griseb.

9347 Chuguiraga erinacea Don

9348 Baccharis gilliesii A. Gray

9349 Senecio subulatus Don ex Hook. & Arn.

9350 Centaurea repens L.

9351 Thelesperma megapotamicum (Spreng.) O. Kuntze

9354 Heterothamus spartioides Hook. & Arn. ex DC.

9355 Baccharis juncea (Lehm.) Desf.

9356 Centauria solstitialis L.

9357 Cyclolepis genistoides Don

9358 Grindelia chiloensis (Corn.) Gabrera

9359 Senecio pampeanus Cabrera

9360 Senecio viravira Hieron.
9361 Gutierrezia solbrigii Cabrera
9362 Baccharis juncea (Lehm.) Desf.
9364 Senecio filaginoides DC.
9365 Chuguiraga hystrix Don
9366 Hyalis argentea Don
9367 Chuguiraga avellanedae Lor.
9368 Senecio subulatus Don ex Hook. & Arn.
9369 Mutisia retrorsa Cav.
9370 Grindelia chiloensis (Corn.) Cabrera
9371 Mutisia spinosa R. & P.
9372 Leuceria achillaeifolia Hook. & Arn.
9373 Haplopappus glutinosus Cassini
9374 Baccharis patagonica Hook. & Arn.
9375 Haplopappus pectinatus Phil.
9376 Baccharis darwinii Hook & Arn.
9377 Baccharis darwinii Hook. & Arn.
9378 Chuguiraga straminea Sandwith
9379 Nassauvia glomerulosa (Lag.) Don
9380 Baccharis rhetinodes Meyen & Walp.
9381 Senecio bracteolatus Hook. & Arn.
9382 Senecio filaginoides DC.
9383 Triptilion achilleae. DC.
9384 Madia sativa Mol.
9385 Nassauvia axillaris (Lag.) Don
9386 Nassauvia glomerulosa (Lag.) Don
9387 Leuceria achillaeifolia Hook. & Arn.

9388 Senecio bracteolatus Hook. & Arn.
9389 Chuguiraga avellanedae Lorentz
9390 Brachyclados megalanthus Spegazzini
9392 Senecio subulatus Don ex Hook. & Arn.
9395 Senecio bergii Hieron.
9396 Senecio subulatus Don ex Hook. & Arn.
9397 Mutisia spinosa Ruiz & Pavon
9398 Baccharis magellanica (Lam.) Pers.
9399 Chiliotrichium rosmarinifolium Less.
9400 Haplopappus paucidentatus Philippi
9401 Nassauvia aculeata (Less.) Poepp. & Endl.
9403 Senecio bracteolatus Hook. & Arn.
9404 Chuguiraga oppositifolia Don
9405 Senecio canchahuinganguensis Cabrera
9409 Grindelia chiloensis (Corn.) Cabrera
9411 Gutierrezia spathulata (Phil.) Kurtz
9413 Dolichlasium lagascae Don
9414 Gutierrezia spathulata (Phil.) Kurtz
9416 Chuguiraga hystrix Don
9417 Chuguiraga rosulata Gaspar
9418 Senecio subulatus Don ex Hook. & Arn.
9419 Heterothalamus spartipides Hook. & Arn. ex DC.
9420 Nardophyllum lanatum (Meyen) Cabrera
9424 Grindelia chiloensis (Corn.) Cabrera
9425 Senecio tricephalus O. Kuntze
9427 Dyssodia pentachaeta (DC) B. L. Robins.
9428 Grindelia boliviana Rusby

9429 Baccharis salicifolia (R.& P.) Pers.

9431 Thelesperma megapotamicum (Spreng.) O. Kuntze

9432 Trichocline sinuata (Don) Cabrera

9433 Heterothalmus spartioides Hook. & Arn.

9436 Chuguiraga erinacea Don

9454 Baccharis salicifolia (R.& P.) Pers.

9455 Proustia cuneifolia Don forma mendocina (Phil.) Fabris

9457 Senecio viravira Hieron.

9459 Baccharis salicifolia (R.&P.) Pers.

9461 Chromolaena arnottianum (Gris.) K & R.

9462 Helenium donianum (Hook. & Arn.) Cabrera

9463 Stevia mercedensis Hieron.

9464 Grindelia boliviana Rusby

9488 centatherum punctatum Cass.

9489 Baccharis punctulata DC.

Not complete and intermixed with others

Some non-Phytochem articles not included

Also none of most recent articles and none of 3 phytologia articles

anning electron microscope studies of the spines and ntioideae (Cactaceae). Amer. J. Bot. 61: 278-283.

n and R. M. Klein 1974b. Hipocrateaceas. In Florula tarina, HIPO 1-30.

binson 1974c. Luziolinae, a new subtribe of oryzoid rey Bot. Club 101: 235-245.

e mosses of Juan Fernandez Islands. Smiths. Contr.

son 1975b. New species of Stomatanthes from Africa sitae). Kew Bull. 30: 463-465.

din-Archbold-Smithsonian Biological Survey of y Dolichopodidae with some related Antillean and (Diptera). Smiths. Contr. Zool. 185: 1-141.

, A. M. Powell, P. H. Raven and H. Robinson 1976a. in Compositae, XIII. Eupatorieae. Ann. Missouri Bot.

sci. In Steyermark, J. A. and C. Brewer-Carias. La vegetacion de la cima del Macizo de Jaua. Bol. Soc. Venezolana Cienc. Nat. 22: 247-249.

_____. 1976c. Hepaticae. In Steyermark, J. A. and C. Brewer-Carias. La vegetacion de la cima del Macizo de Jaua. Bol. Soc. Venezolana Cienc. Nat. 22: 249-261.

Smith, L. B., J. A. Steyermark and H. Robinson 1976d. Navia jauana, Navia luzuloides and Navia scirpiflora. In Steyermark, J. A. and C. Brewer-Carias. La vegetacion de la cima del Macizo de Jaua. Bol. Soc. Venezolana Cienc. Nat. w2: 287-290, 307-310.

Bohlmann, F., C. Zdero, R. M. King and H. Robinson 1977a. A new ageratone derivative from Isocarpha oppositifolia. Phytochemistry 16: 768.

King, R. M. and H. Robinson 1977b. Compositae in Flora of Guatemala: a review. Taxon 26: 435-441.

_____ and _____. 1977c. Guayania davidsei and Hebeclinium gentryi, new species from northern South America (Eupatorieae-Asteraceae). Ann. Missouri Bot. Gard. 64: 366-370.

Robinson, H., L. B. Holm-Nielsen and B. Løjtnant 1977d. Mosses of Ecuador II. Lindbergia 4 (1-2): 105-116.

Robinson, H. 1977e. An analysis of the characters and relationships of the tribes Eupatorieae and Vernonieae (Asteraceae). Syst. Bot. 2: 199-208.

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Smith, L. B., H. Robinson and R. M. Klein 1974b. Hipocrateaceas. In Florula da Ilba de Santa Catarina, HIPO 1-30.

Terrell, E. E. and H. Robinson 1974c. Luziolinae, a new subtribe of oryzoid grasses. Bull. Torrey Bot. Club 101: 235-245.

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Robinson, H. 1975. Bredin-Archbold-Smithsonian Biological Survey of Dominica: The family Dolichopodidae with some related Antillean and Panamanian species (Diptera). Smiths. Contr. Zool. 185: 1-141.

King, R. M., D. W. Kyhos, A. M. Powell, P. H. Raven and H. Robinson 1976a. Chromosome numbers in Compositae, XIII. Eupatorieae. Ann. Missouri Bot. Gard. 63: 862-888.

Robinson, H. 1976b. Musci. In Steyermark, J. A. and C. Brewer-Carias. La vegetacion de la cima del Macizo de Jaua. Bol. Soc. Venezolana Cienc. Nat. 22: 247-249.

_____. 1976c. Hepaticae. In Steyermark, J. A. and C. Brewer-Carias. La vegetacion de la cima del Macizo de Jaua. Bol. Soc. Venezolana Cienc. Nat. 22: 249-281.

Smith, L. B., J. A. Steyermark and H. Robinson 1976d. Navia jauana, Navia luzuloides and Navia scirpiflora. In Steyermark, J. A. and C. Brewer-Carias. La vegetacion de la cima del Macizo de Jaua. Bol. Soc. Venezolana Cienc. Nat. w2: 287-290, 307-310.

Bohlmann, F., C. Zdero, R. M. King and H. Robinson 1977a. A new ageratone derivative from Isocarpha oppositifolia. Phytochemistry 16: 768.

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Robinson, H. 1977e. An analysis of the characters and relationships of the tribes Eupatorieae and Vernonieae (Asteraceae). Syst. Bot. 2: 199-208.

Q.37-7
(Rev. 12-54)

UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Service
Plant Quarantine Branch
209 River Street, Hoboken, N. J.

MATERIAL REQUIRING DEFOLIATION

Because of the risk of introducing citrus blackfly (Aleurocanthus woglumi), plants and cuttings of the following genera from all sources except Canada, Europe, Asia Minor, and Mediterranean Africa, must be defoliated before shipment if they are to be entered through any port other than New York, N.Y. (including Hoboken, N.J.). Defoliation is not required when plants and cuttings of these genera enter directly through the port of New York for plant quarantine clearance.

Achras
Anacardium
*Annona
Ardisia
Bouvardia
Bumelia
Bursera
Buxus
Calocarpum
Capsicum
Cardiospermum
Cedrela
Cestrum
Cnidoscolus
Coffea
**Crataegus
*Cydonia
*Diospyros
Duranta
Eugenia
**Fraxinus
**Hibiscus
Hura
Ixora
Jatropha
Lagerstroemia
*Lucuma
Magnolia
*Mammea
*Mangifera
Melia
Myroxylon
Myrtus
Parmentiera
*Persea
Plumeria
**Populus
*Psidium
*Punica
**Pyrus
Sapindus
Solandra
Spondias
Strelitzia
Tabebuia
**Vitis
Zingiber

*Species of commercially cultivated fruits or nuts are subject to postentry quarantine.

**See Quarantine 37 for countries from which prohibited or subject to postentry quarantine.

MATERIAL ARRIVING IN FOLIAGE contrary to the provisions of this circular will be refused entry and immediately become subject to the application of such safeguards as may be deemed necessary and prescribed by the inspector to prevent possibility of pest escape, including confiscation and immediate destruction if in the opinion of the inspector the circumstances warrant.

Import and Permit Unit

Q.37-12
(Rev. 6-55)

UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Service
Plant Quarantine Branch
209 River Street, Hoboken, N. J.

TROPICAL PLANTS NOT SUBJECT TO PROHIBITIONS OR SPECIAL RESTRICTIONS

Listed below are a considerable number of plant genera of a tropical or subtropical nature enterable under permits issued for "Admissible tropical plants not subject to special restrictions", or under permits issued for "Admissible nursery stock not subject to postentry quarantine". The following list does not include the bulb genera listed in Circular Q.37-3. Plants of the families Araceae and Bromeliaceae are grouped as "Aroids" and "Bromeliads". Ferns, cacti, and succulents are also listed by group name only. When the permittee or applicant has only a common name he should learn from a competent horticultural authority or source the scientific name of the plant. If the generic name appears in the list below without any qualifications it will be understood that all of the species of the genus are enterable. For example, Aralia spinosa, Aralia cordata and all other species of the genus Aralia are enterable.

Genera marked with an asterisk (*) consist entirely of species of woody plants or contain certain species which are woody. Regulation 18 (d) of Quarantine 37 requires that species of woody plants which can be grown from and come true from seed must be imported in the form of seed rather than plants unless it can be shown that it is impossible or impracticable to import viable seed. Varietal material of these woody species, that is, material which may be produced only by budding, grafting, layering or by cuttings may be imported.

Genera marked with a number sign (#) from all sources except Canada, Europe, Asia Minor, and Mediterranean Africa, must be defoliated before shipment if they are to be entered through any port other than New York, N. Y. (including Hoboken, N. J.).

*Abrus
*Abutilon
*Acalypha
Acanthus
*Achania
(Malvaviscus)
*#Achras
Achyranthes
*Aeschynanthus
Agave
*Albizzia
*Allamanda
Alpinia
Amomum
*#Anacardium
Angelonia
Anthericum
Antigonon
*Aralia
*Araucaria
*#Ardisia
Argemone
*Aristolochia
Aroids
(Except Anthurium)
*Artocarpus
Aspidistra
*Aucuba
*Barleria
Bassia
*Bauhinia
*Beaumontia
Beloperone
*Bertolonia
*Bougainvillea
*#Bouvardia
*Breynia
Bromeliads
(except to Hawaii)
*Brunfelsia
(Franciscea)
Cacti
*Callistemon
*#Calocarpum
*Calophyllum
Canna
*Carissa
*Cassia
*Ceropegia
*#Cestrum
*Chorizema
Cissus
Cleome
*Clerodendron

Clitoria
Clivia
*Clusia
*Coccolobis
*Cocculus
*Codiaeum
*Coprosma
Cordyline
*Crossandra
*Cryptostegia
[redacted]
*Dipladenia
*Dizygotheca
(Aralia)
*Dodonaea
*Dombeya
Dracaena
*#Duranta
*Durio
*Elaeagnus
Episcia
*Eranthemum
*Erythrina
*#Eugenia
*Euphorbia
*Eurya
*Fatsia
(Aralia)
Ferns
*Firmiana
Fittonia
*Franciscea
(Brunfelsia)
*Franklinia
(Gordonia)
*Galphimia
(Thryallis)
*Gardenia
*Gordonia
(Franklinia)
*Graptophyllum
*Grevillea
Heliconia
*Higginsia
(Hoffmannia)
*Hoffmannia
*Hoya
Hunnemannia
*Indigofera
*Inga
Iresine
Isoloma
*#Ixora
*Jacaranda
*Jacobinia
*#Jatropha
*Justicia
*#Lagerstroemia
*Lantana
Lapageria
*Laurus
Ligularia
*Lonicera
*#Magnolia
Malvastrum
*Malvaviscus
(Achania)
*Manettia
Maranta
*Marcgravia
Marica
Maurandia
*Medinilla
*#Melia
*Mimosa
*Muehlenbeckia
Musa
*#Myrtus
*Nandina
Nepenthes
*Nerium
Orchids
(Except to Hawaii)
*Osmanthus
Pandanus
*Pandorea
*Parkinsonia
*Pedilanthus
Peperomia
*Petrea
Phormium
Pilea
*Piper
*Pittosporum
Plumbago
*#Plumeria
*Poinciana
*Poinsettia
*Polyscias
(Aralia)
Porana
*Quisqualis
Rhoeo
*Rhynchospermum
(Trachelospermum)
*Russelia
Saintpaulia
*Sanchezia
Sansevieria
Saxifraga
*Schefflera
*Schinus
*#Solandra
*Sparmannia
*Spathodea
*Sphaeralcea
*#Spondias
Stapelia
*Stephanotis
#Strelitzia
*Strobilanthes
Succulents
*#Tabebuia
*Tabernaemontana
*Tamarix
*Tecoma
*Thespesia
*Thevetia
*Thryallis
(Galphimia)
*Thunbergia
*Tibouchina
*Trachelospermum
(Rhynchospermum)
Tradescantia
(Zebrina)
Tree Ferns
*Trichostigma
*Vinca
Zebrina
(Tradescantia)
#Zingiber

[redacted] Permit Unit

MOLECULAR SYSTEMATICS OF SENECIONEAE (COMPOSITAE)

HINTS FOR COLLECTORS OF STUDY MATERIAL

Introduction

As part of a multidisciplinary study of the systematics of the tribe Senecioneae (Compositae) worldwide, Professor Joachim W. Kadereit (University of Mainz), in cooperation with myself and Professor Bertil Nordenstam (Natural History Museum, Stockholm), will be undertaking a program of molecular systematics using cpDNA. We are anxious to secure the cooperation of all those willing to collect study material and send it to him. If you or any of your colleagues are able to help in this way, either in your locality or botanic garden, or on expedition elsewhere now or in the future, we should be most grateful.

I enclose a copy of list of the genera of the tribe (and sections of Senecio) to be found in your region of the world. Lists are available for the following regions: Europe, N Africa & N Asia; SW & central Asia & the Caucasus; Macaronesia; E Asia; Indian subcontinent & Indochina; Malesia; Australasia & the Pacific; tropical & S Africa; Madagascar & the Mascarene Is; N America & Mexico; Central America & W Indies; W tropical S America; E tropical S America; and temperate S America. They can be sent on request.

General

As air-dried material does not consistently yield intact DNA, please collect seeds or fresh leaf tissue. Dried leaf material should be sent only if one is in a remote collecting area unlikely to be revisited by collectors and no express mail service is available.

Corresponding voucher herbarium material should be collected for each sample of study material. Please send one voucher specimen for verification to The Director, Royal Botanic Gardens, Kew, Richmond, Surrey TW9 3AE, marked "for the attention of Mr. C. Jeffrey".

It is essential that the export regulations of the country in which you are collecting, appropriate to the kind of material being sent, are strictly observed. Please familiarize yourself with them beforehand, ensure the correct procedures are followed and the necessary documentaion provided. It is especially important to ensure that no delay will occur in the transport of fresh material.

Addressing of consignments

Please address all consignments clearly to: Professor J. W. Kadereit, Institut für Spezielle Botanik und Botanischer Garten, Johannes Gutenberg-Universität Mainz, Postfach 3980, Saarstrasse 21, 8500 Mainz, Germany, and mark the packet "SENECIONEAE" on the outside.

Seeds

Ripe, air-dry seeds (achenes) should be placed in paper envelopes and sent by air mail.

Living material (succulent species)

Place c. 10 g fresh leaf or green stem material, with suitable dry packing, into a small cardboard box and send samples by air mail.

Living material (non-succulent species)

Seal 4-6 g of fresh leaf material into a ziplock or similar plastic bag.

Enclose sample or samples in a suitable styrofoam shipping box, together with a small handfull of ice double-sealed in plastic bags to act as thermal buffering.

Send by international express courier (e.g, DHL, TNT) with collection time pre-arranged to avoid delay. To avoid possible customs difficulties, consignments must be routed to enter Germany at Frankfurt-am-Main airport.

Send early in the week (e.g., Monday or Tuesday) to avoid possible delays at weekends.

If possible phone (061 31 39 2533) or fax (+49 6131 393 524) Prof. Kadereit to inform him of time of despatch and courier responsible.

Air-dried material

Please collect for rare or local genera (and sections of Senecio), especially if endemic to the area visited, and no other method is possible. Use preferably the silica gel method as described by M. W. Chase & H. H. Hills in Taxon 40: 215-220, 1991, otherwise simple airdrying. For further information, contact C. Jeffrey at the Kew address given above.

Postal expenses

If you require refund of postal expenses, please enclose an invoice (giving bank, account number etc) with your consignment. We regret that packaging materials cannot be provided, but those used will be returned if return is requested.

C. Jeffrey

purposes. In Peru, it is known as "ajenjo," a name also used for the genus *Ambrosia*.

JUNÍN. Jauja: Jauja, *Cerrate 3810* (MO).

2. **Artemisia annua** L., Sp. Pl. 847. 1753. TYPE: Siberia, exact locality and collector unknown (LINN, holotype, not seen, IDC Microfiche 117. 566: II. 4).

Erect **annuals** to 2 m tall; stems puberulous to glabrous, reddish. **Leaves** ovate in outline, 2–3-pinnatifid, sessile, the basal segments 3–10 mm long, deeply toothed, remote from next distal pair, median segments 3–4 cm long, regularly and deeply toothed, the ultimate lobes linear-lanceolate, 1–5 mm long, 0.5–1.0 mm wide, glabrous. **Inflorescences** paniculate. **Capitula** disciform, heterogamous, 1.5–3.0 mm high, 2.0–3.5 mm wide, pedunculate, often nodding; involucres globose; phyllaries 2–3-seriate, graduate, the outer oblong, herbaceous, ca. 0.6 mm long, the inner ovate-oblong, mostly scarious, ca. 2 mm long, 1.5–2.0 mm wide; receptacles naked; florets 20–25, the outer pistillate, fertile, the corollas filiform, to 1 mm long, the inner florets hermaphroditic, fertile, the corollas cylindric-campanulate, 0.6–1.0 mm long, all yellowish, glabrous. **Achenes** narrowly turbinate, ca. 0.8 mm long, obscurely striate. Chromosome number: $n = 9$.

This species is a native of Asia and is widely naturalized in central and southern Europe and throughout the New World. In Peru, it is represented by cultivated material only.

JUNÍN. Jauja: Jauja, *Ridoutt s.n.* (MO).

III. CHRYSANTHEMUM

Chrysanthemum L., s.l., Sp. Pl. 887. 1753. TYPE: *C. coronarium* L.

Annual **herbs,** glabrous or pubescent, often strong scented. **Leaves** alternate, the margins entire, toothed, incised or variously dissected, pubescent or glabrate. **Inflorescences** solitary or 2–5 on branch tips, often long pedunculate. **Capitula** radiate, heterogamous; involucres hemispherical or campanulate; phyllaries 3–4-seriate, imbricate, the margins scarious, the costa darkened; receptacles convex, epaleate; ray florets 13–21(-34), the ligules entire or dentate, pistillate, usually fertile, white or yellow, and rarely with reddish bases; disc florets 50–200, hermaphroditic, fertile, the corollas yellow, the tube laterally expanded and 2-winged, the anthers basally obtuse or truncate, the terminal appendage ovate, acute, the style branches narrowly oblong, truncate, penicillate. **Achenes** without vallecular secretory canals or epicarpic mucilaginous cells, those of the ray florets 3-angled, with the ribs often winged, those of the disc florets cylindrical to cylindrical-triquetrous, ribbed, the adaxial rib sometimes winged; pappus absent.

The genus *Chrysanthemum*, when interpreted in a broad sense, includes about 200 species, mainly natives of Europe, western Asia, and northern Africa, with species naturalized on nearly every continent. Considerable biosystematic evidence indicates that this genus has been quite heterogeneous, and recent workers (Heywood & Humphries, 1977) have recircumscribed the generic limits, thus limiting the genus to a group of three species: *C. carinatum*, *C. coronarium*, and *C. segetum*, all of northern Africa and Europe. These changes have been reflected in several recent floras (e.g., *Flora of Turkey*, 1975; *Flora Europaea*, 1976). In the present treatment, several taxa traditionally treated under *Chrysanthemum s.l.* are treated under other genera (cf. *Tanacetum*, *Dendranthema*, and *Leucanthemum*).

REFERENCES

Grierson, A. J. C. 1975. *Chrysanthemum*. *In* Davis, P. H. (ed.), Flora of Turkey. **5:** 253–255.
Heywood, V. H. 1976. *Chrysanthemum*. *In* Tutin, T. G., et al. (eds.), Flora Europaea. **4:** 168–169.

Heywood, V. H., and C. J. Humphries. 1977. Anthemideae—Systematic review. *In* Heywood, V. H., et al. (eds.), The Biology and Chemistry of the Compositae, pp. 852–898. Academic Press, London.

1. **Chrysanthemum coronarium** L., Sp. Pl. 890. 1753. TYPE: Europe, exact locality and collector unknown (LINN, holotype, not seen, IDC Microfiche 117. 603: II. 3).

Annual **herbs** to 0.75 m tall; stems erect, glabrous. **Leaves** oblong to obovate in outline, 2–3-pinnatifid, to 5 cm long, 2–3 cm wide, sessile, the ultimate segments 1–2 mm wide, acute. **Inflorescences** solitary; peduncles 5–15 cm long, ebractate. **Capitula** ca. 1 cm high, 1.0–1.5 cm wide (excluding rays); involucres hemispherical; phyllaries 3-seriate, ovate-oblong, 5–10 mm long, 3–5 mm wide, the margins scarious, brownish; ray florets ca. 21(-34), the ligules 1.0–1.5 cm long, ca. 5 mm wide, yellow, cream, or white; disc florets 50–100, the corollas 4–5 mm long, yellow. **Achenes** dimorphic, the outer triquetrous, the angles produced into wings to 1.5 mm wide, the inner laterally compressed with adaxial wings, prominent ribs on abaxial face and rounded ribs on lateral faces, sometimes those of the center lacking wings, all covered with sessile, non-mucilaginous glands. Chromosome number: $n = 9$.

This species is native to the Mediterranean region and is now a widespread weed in many temperate areas. In Peru, it is cultivated for ornament and often escapes to roadsides and waste places.

JUNÍN. Jauja: Jauja, *Ridoutt s.n.* (MO). CUZCO. Anta: Chaccan Chico, El Chaccan, 3,490 m, *Brunel 484* (MO).

IV. COTULA

Cotula L., Sp. Pl. 891. 1753. TYPE: *C. coronopifolia* L.

Annual or perennial **herbs,** often diminutive, prostrate to decumbent, often rhizomatous or stoloniferous, glabrous to pilose, often with pellucid glands. **Leaves** alternate, 2–3-pinnatifid, rarely simple, toothed to entire, petiolate or not, the bases amplexicaul or only partly so. **Inflorescences** solitary, terminal and axillary; peduncles sometimes swollen under the capitula. **Capitula** monoecious, dioecious, or gynomonoecious, disciform, heterogamous; involucre hemispherical to campanulate; phyllaries 2–many-seriate, subequal, herbaceous, scarious at least marginally; receptacles conical, flat or convex, rarely hemispherical; epaleate; marginal florets pistillate, 1–many-seriate, the corollas filiform, sometimes 2-toothed or with a minute ligula (sometimes corollas lacking); disc florets hermaphroditic, fertile, or functionally male, the corollas cylindric-campanulate, funnelform, or tubular, sometimes with the bases sheathing and extending over the ovary, 4-lobed (rarely 3-lobed), the anthers 4 (rarely 3), basally obtuse or minutely tailed, the terminal appendage ovate or lanceolate, the style branches of the marginal florets linear-lanceolate, of the disc florets oblong, truncate, penicillate. **Achenes** generally stipitate, terete, or dorsally compressed, winged or not, dorsally convex; pappus absent.

About 90 species, almost cosmopolitan, but mainly South African and in New Zealand, some in North America, Asia, Australia, New Guinea, South America, and the Falkland Islands.

REFERENCE

Caro, J. A. 1961. Las especies de *Cotula* (Compositae) del centro de la Republica Argentina. Kurtziana **1:** 289–298.

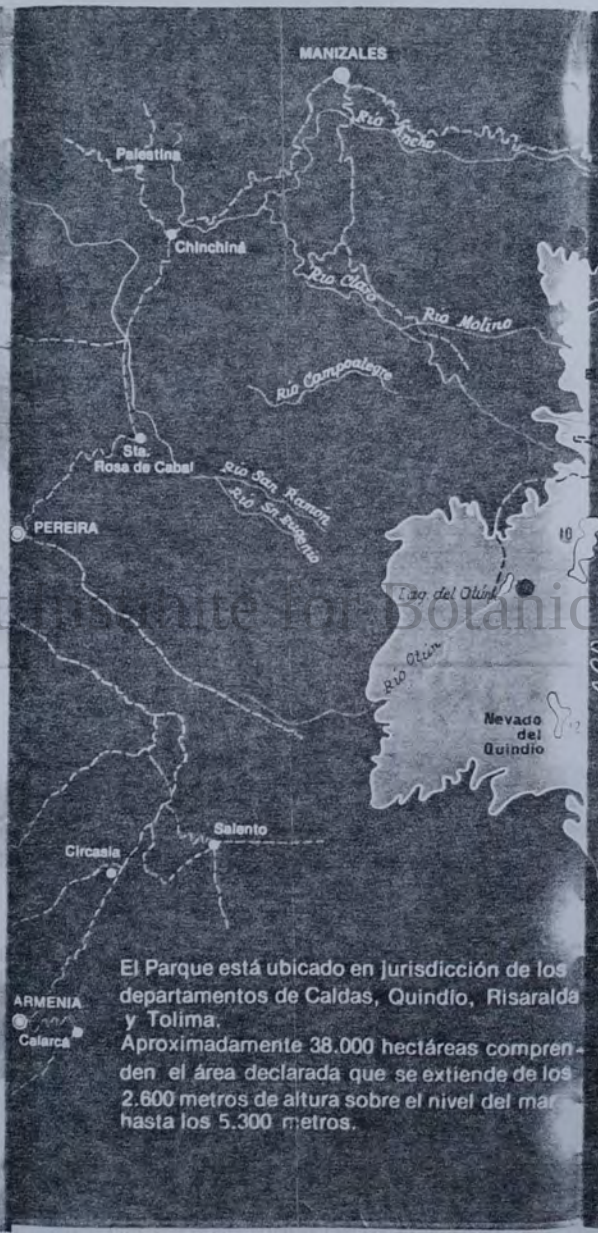
Key to Species of *Cotula*

1. Receptacle pilose; disc corollas 3-lobed, stamens 3; achenes isomorphic ..... 3. *C. mexicana*.

ALGUNOS SITIOS DE MAYOR INTERES

- **TERMALES DEL RUIZ:** Piscina de agua azufrada, hotel y Restaurante.
- **CASCADA DEL RIO GUALI:** Hermosa cascada sobre una pendiente de roca andesítica.
- **LOS ESTRATOS:** Magnífica exposición de los suelos fósiles del Parque en un corte de la carretera.
- **LAS CHARCAS:** Sitio de un gran lahar que llenó el Valle.
- **VOLCAN NEVADO DEL RUIZ:** Altura 5.300 metros.
- **EL REFUGIO:** Hotel y Restaurante.
- **CRATER DE LA OLLETA:** Viejo cono volcánico.
- **VOLCAN NEVADO DEL CISNE:** Altura 5.100 metros.
- **LAGUNA VERDE:** Al sur del nevado del Cisne Pequeño Lago de origen glacial.
- **VOLCAN NEVADO DE SANTA ISABEL:** Altura 4.965 metros.
- **LAGUNA DE OTUN:** Hermosa laguna resultado de bloques de un Valle glacial por un derrame hidro-volcánico.
- **VOLCAN NEVADO DEL QUINDIO:** Altura 4.800 metros.
- **VOLCAN NEVADO DEL TOLIMA:** Altura 5.215 metros.
- **QUEBRADA ALFOMBRALES:** Escenario geológico donde se evidencian trazas de reciente glaciación.
- **TERMALES DEL RANCHO:** Azufradas con piscinas, cabañas de sauna, salas de pernoctar y restaurantes.

CENTRO DE INVESTIGACIONES
BIO - ECOLOGICAS



El Parque está ubicado en jurisdicción de los departamentos de Caldas, Quindío, Risaralda y Tolima.
Aproximadamente 38.000 hectáreas comprenden el área declarada que se extiende de los 2.600 metros de altura sobre el nivel del mar hasta los 5.300 metros.

PARQUE NACIONAL NATURA
LOS NEVADOS

Escala Aproximada 1: 125.000

I. Parque Nacional Natural Isla de Salamanca
11°06'N, 74°22' E
0-8 m. alt, 21,ooo hectares
mangles: Laqunoularia racemosa, Rhizophora mangle, Avicennia nitada
Tropical dry forest with Prosipis juliflora and Pereskia sp.
Between Barranquila and Santa Marta. One of richest areas in world for birds. Rafeal Romero Castañeda, 1971 wrot "Flora de la Isla de Salamanca.
Local administrator: Nestor Mijia Pizarro, Ing. Forestal, Carrera 44, No. 40-20, Piso 9°, INDERENA, Barranquilla, Dpto del Atlantico, Colombia, S.A.
I heard a rumor that this park was to be paved over, but not certain.

II. Parque Nacional Natural Tayrona
20°12' lat N, 73 53' E, Northeast of Santa Marta.
Alt. 0-1ooo m., 15,ooo hectares.
Beach, coral reef, fish, archeological relics of Tayrona culture.
Virgin forst with Aematoxilon, Anacardium excelsum, Hura crepitans, Ficus spp, Sabal mauritiformis, Coccoloba condolleana, etc.
Green turtle Chlonia mydas
Classified as Monte Espinoso lTropical to Bosque Hum ido Tropical.
Publication:"Estudios de investigaciones sobre vegetaciòn, reconocimiento de areas corlinas y avifauna" by Corp. del Valle del Magdalena y INDERENA '68, '69, '70, '71
Administrator: Ingeniero Jefe del Proyecto Parque Nacional Natural Tayrona, Calle 11, No. 3-45, INDERENA, Santa Marta, Dpto del Magdelena, Colombia, SA.

III. PNN Sierra Nevada
10°54' lat. N, 73°27' long. E.
3,000-5,780 m. alt., 50,000 hectares.
This is hiest alt, in Colombia; Pico Simón Bolivár. The Arhuaca tribe lives there.
Paramo, glacier, cocks. Many endemic species. Espeletia glossophylla, E. suberiifolia. NO FACILITIES.

IV. PNN Purace 2°25' lat. 76°14' long.
3,000 2,500-4700 m. alt. Southeast of Popayán. Busque humido subtropical to bosque muy humedo. Montaño Bajo.
Quercus, Compositae, Ericaceae, Espeletia hartwegiana
Admin: Heliodoro Sanchez Paez, Ing. Forestal, Calle 4a, No4-38, INDERENA, Popayán, Dpto del Cauca, Colombia SA
(Big earthquake in Popayán recently. Probably the administrations upset. Lovely park, though, rains all the time and cold. There's a shelter there possibly for scientists, but if not there's a tourist motel down the road a few miles.)

V. PNN Cueva de los Cuacharos
1,700 - 4,000 m. alt, 700 hectares.
SE of Neiva, Dpto del Itaila
Caves, birds. Bosque muy humedo subtropical to Bosque humedo subtropical.

Colombian pines, Podocarpus spp, "romerón" and "Hayuelo".Cedros "Cedrela" , Juglans spp, "Nogales" palms, orchids, monkeys, birds. Alfredo del Castillom Ing. Forestal Jefe del Proyecto, INDERENA, Pítalito, Dpto del Huila, Colombia, SA.

VI. PNN La Macarena
3°17' Lat N. , 72°46' Long. E. SE of Villavicencio City
250-2500 m. alt, 600,000 hectares
Bosque humedo tropical to Bosque Pluvial Subrropical.
Humberto Arturo Hermida A., Ing. Forestal, Jefe del Proyecto, Calle 36 No. 29-47, INDERENA, Villavicencio, Dpto del Meta, Colombia, SA.

VII. PNN Los Nevados
4°45'Lat N., 75°12' Long E.
2600-5400 m. alt.
Quercetum tolimense "roble","Encenillos" Weimannietum, Clethraetum, Vaccinetum, Ceroxylon (!!!) ,
Humeda y Muy Humeda de la Faja Montano Bajo ,
Muy Humeda y Pluvial de la Montano, Paromo,
Pluvial subandino, Tundra Pluvial Andina
Gustav Sanchez H, Jefe del Proyecto, Calle 20, No 2120, A.A. 721, Manizales, Colombia (This is recent address, summer"82)
Dr. Sanchez enthusiastically encouraged visiting scientists. He advises that we write directly to him and to avoid correspondence with Inderena in Bogotá or wherever they're centered. He can provide transportation from Manizales to the park, and there are facilities where visiting scientists (not tourists) can stay. BRING YOUR OWN FOOD. THERE's NOTHING TO BUY BUT COCOA AND CHEESE ONCE YOU"VE ENTERED THE PARK.

VIII PNN Las Orquideas
6°41' N lat, 76°24' WLong. Antioquia
300-3,850 m. alt, 3200 hectares. Bosque Humetro Tropical (8000mmrain) to Bosque Pluvial subropical, Bosque Pluvial Montano Bajo
Ing. Jefe del Proyecto Parque NN Las Orquideas, Calle 54, Caracas No 45-81, INDERENA, Medellin, Colombia S.A.

IX PNN Los Katios
7°58' Lat N, 77°08" Long E. 5-600 m. alt., 52,000 hectares.
Pan Am hiway near Panama border. Ing. Forestal, Jefe del Proyecto PNN Los Katios, INDERENA, Turbo. ,Dept de Antioquia, Colombia SA

X. Territorio Faunistico El Tuparro. 5°35' Lat N, 67°48'Long E
75-250 m. alt, 38,000 hectares. Tribes :Guahibos, Cuivas and Sálibas
30°C, 2000 mm rain/yr. Tabebuiaspp., Guarea spp, Hymenaea courbaril Pseudo samanea, guachapele "Igua", Curatella americana, Cedrela Acrocomia sp, Jessenia polycarpa, Andropogon bicorne, Mauritia flexuosa. Calle 36,No 29-47, INDERENA, Villavicencio, DPto de Meta, Colombia.
Pub."Formaciones Vegetales de Colombia", Dpto Agrologico, Inst. Geografico, :"Augustín Codazzi", Bofotá, D.E. 1963

Names & Addresses may help:

Pedro Antonio Cano Villegas, Carrera 1, No 10-15, Buga, Valle. I think he's moved recently, so possibly write to him c/o Germen Parra V, Carrera 22, No 36A14, Palmira, Valle, Colombia.

Pedro is a high school chemistry teacher very interested in anything having to do with ecology. He's very intense, but a good friend to have. He has influence with Dr. Sanchez at the Parque Nacional Natural Los Nevados and would probably go along on any trip you might take there.

Dra. Melida de Froume, Decana de Agronomia, Universidad de Caldas, Manizales, Colombia.

-this woman is dean of Dpt of Agronomy. Her thesis project was done on "plants of the paramo" at PNN Los Nevados. I don't think she goes into the field anymore, but perhaps she could assist on e by opening up the herbarium at the University, as she did for us.
, (also for letters of permisstion for collecting)

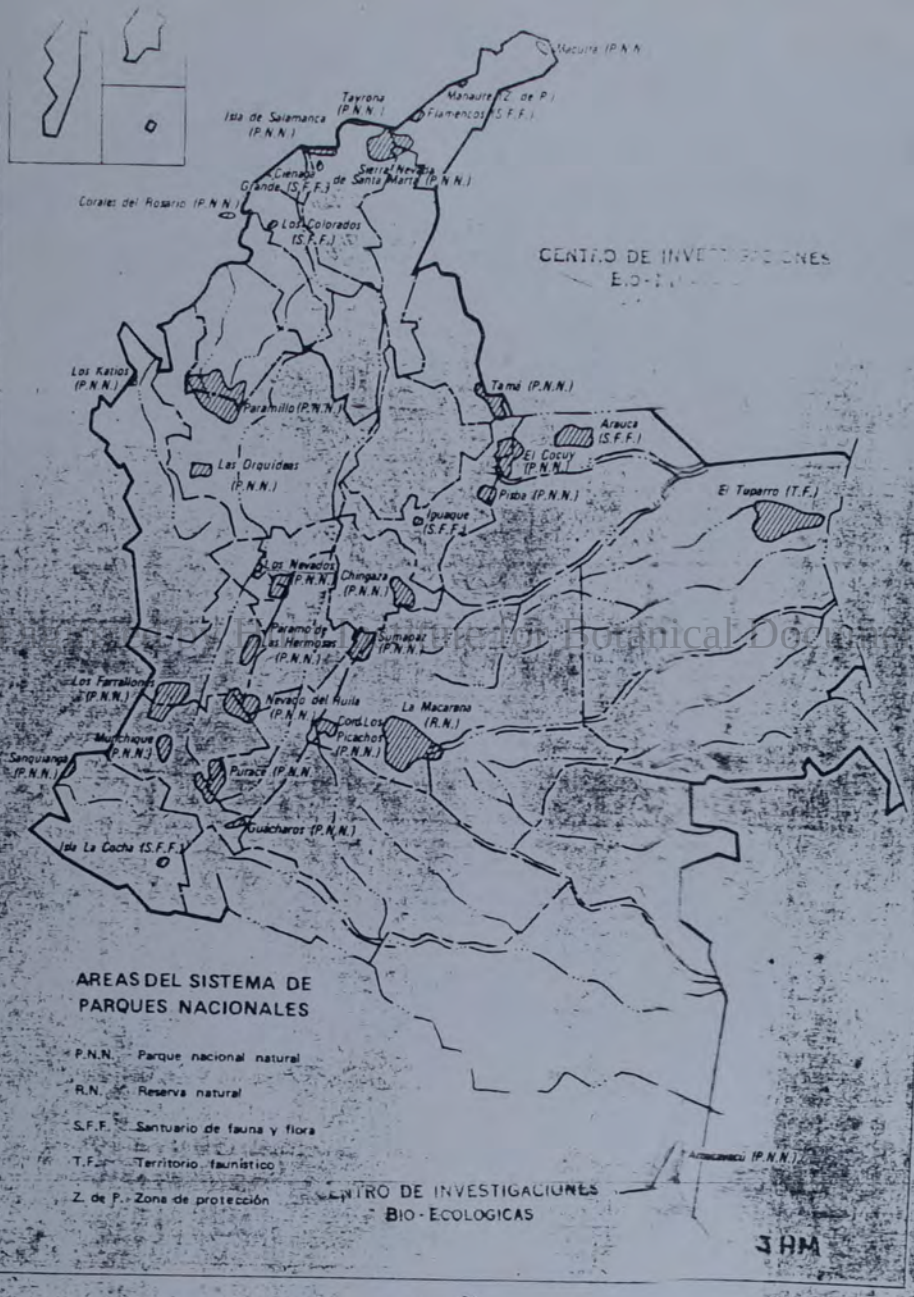
Dr. Philip Silverstone, Jefe, Seccion de Botanica, Dpto de Biologia, Univ. del Valle, A.A. 2188, Cali, Valle, Colombia S.A.
-he's an American herpetologist-turned botanist.There are nice dryer facilities at the University.

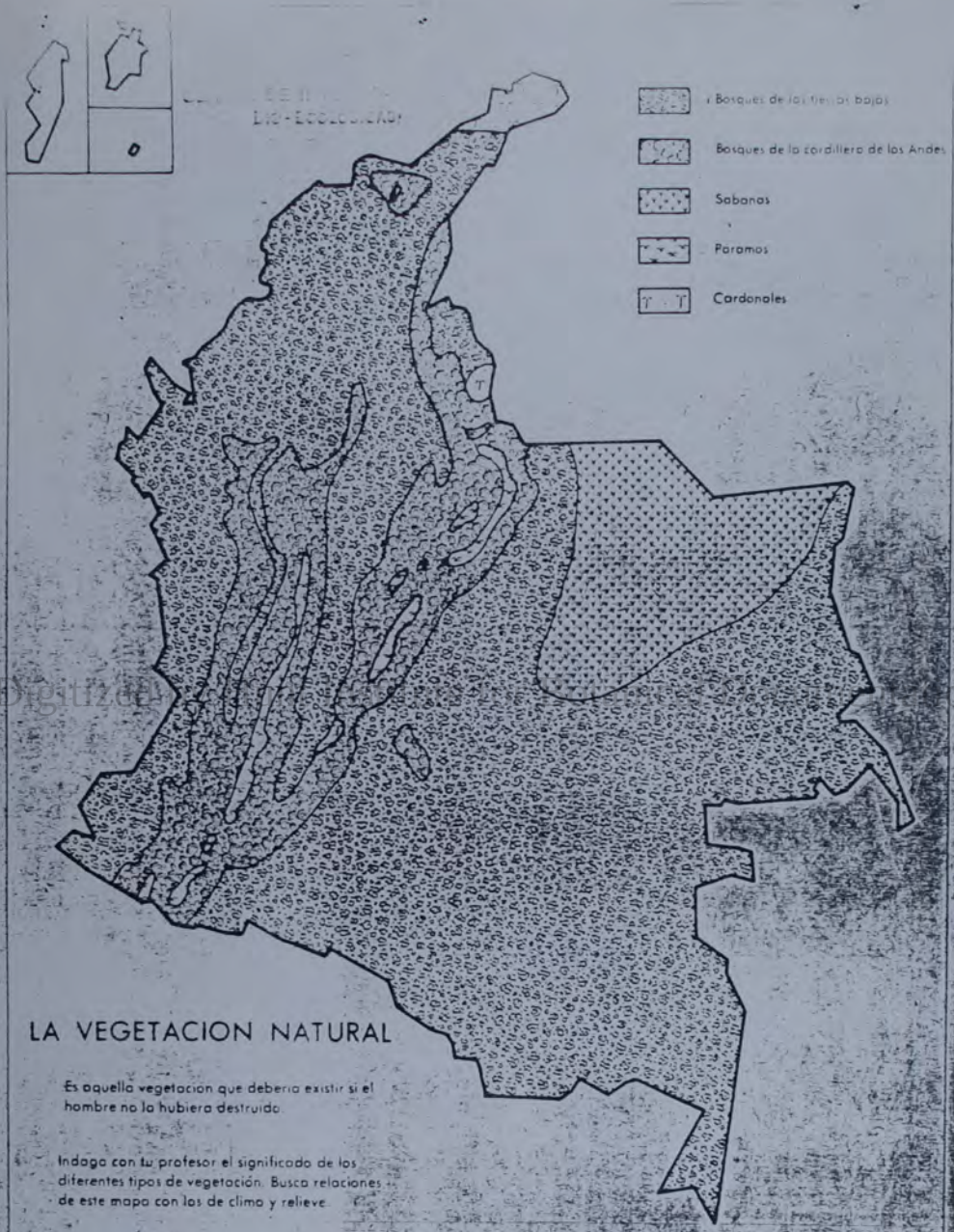
Isidoro Cabrera-curator of Univ Valle herbarium. Most helpful
Eugenio Escobar-curator of Univ. Nacional de Palmira herbarium. (see herbarium index for address) Very willing to help, has small dryers and an assistant,a regualr museum of Cuatrecasas' collection.

William Ladrach- some position at Carton de Colombia, American. He can arrange to have specimens sent out of the country without your getting a permit from INDERENA. I've lost his address, but a cable or address can be found by looking up Carton de Colombia, Cali, Colombia. His assistant, Humberto Mazvera, takes care of all the actual arrangements and his phone number in Cali is 417922.

Victor Patiño- I've given up on him, but it's worth a try for you. He's not very good at getting specimens out of the country, as I understand, so if you can get jeep use , lodging in Cali, and letters of permission for collection from him you've done well .

Adrian Juncosa, Dept of Botany Duke Univ, Durham, NC 27706
- was collecting in Choco area from Nov '82 to Apr '83
- is at Harvard, Dept of Anatomy for summer, then will return to Choco for a while, after which has grant @ Harvard.



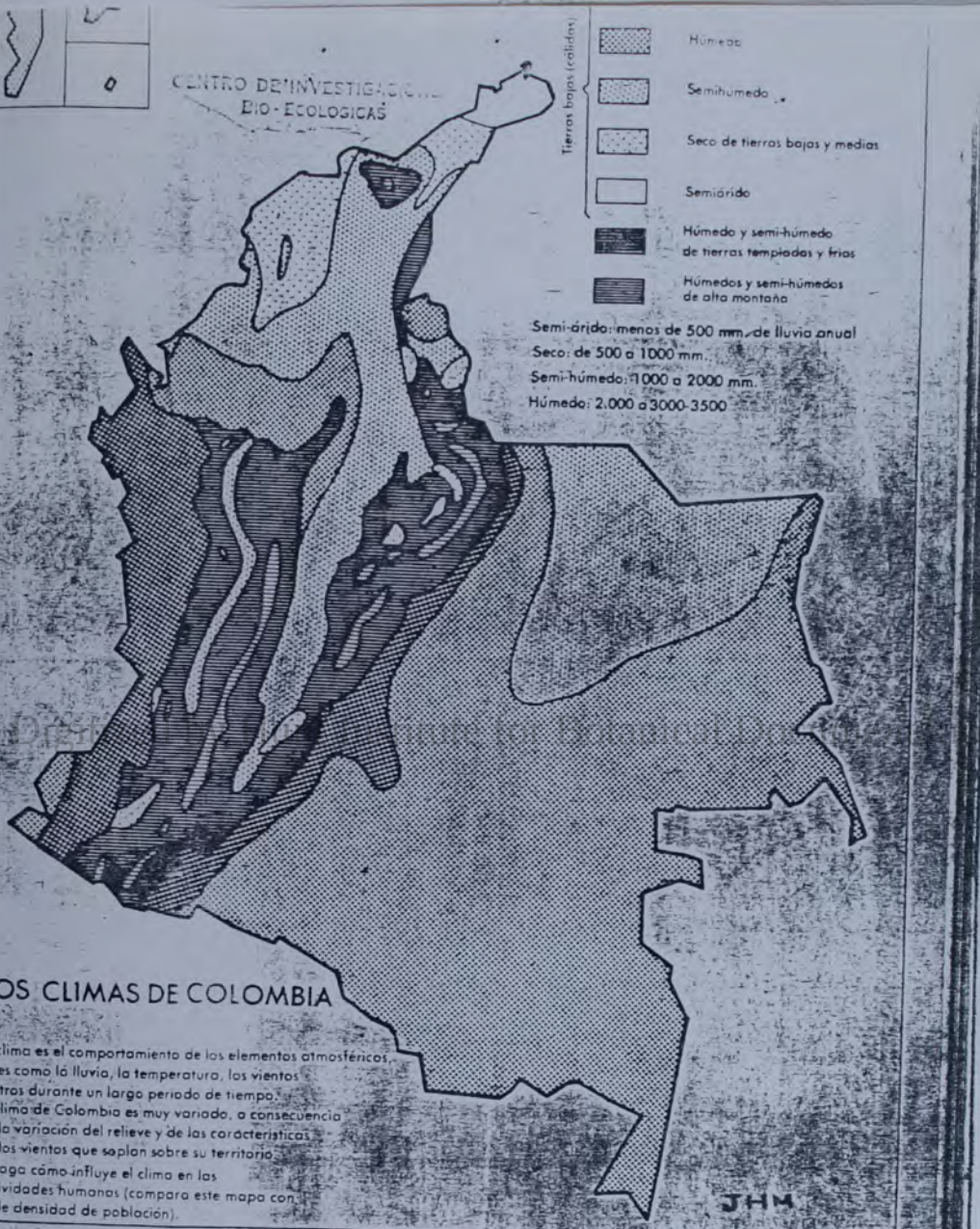


LA VEGETACION NATURAL

Es aquella vegetacion que deberia existir si el hombre no la hubiera destruido.

Indaga con tu profesor el significado de los diferentes tipos de vegetación. Busca relaciones de este mapa con los de clima y relieve.

JHH



LOS CLIMAS DE COLOMBIA

El clima es el comportamiento de los elementos atmosféricos, tales como la lluvia, la temperatura, los vientos y otros durante un largo periodo de tiempo.
El clima de Colombia es muy variado, a consecuencia de la variación del relieve y de las características de los vientos que soplan sobre su territorio.
Indaga cómo influye el clima en las actividades humanas (compara este mapa con el de densidad de población).

ISA PARTS S. A.

AV. IQUITOS 221 - 227
TELF. 311949

SEÑOR .....

VENTA AL CONTADO Nº 122523

Cant.	DESCRIPCION	S/. VALOR UNITARIO	S/. VALOR Reb. D.L. 19256	VALOR NETO	SUB - TOTAL	D. L. 19256 TASA	D. L. 19256 TOTAL
2	Monzol 1000 shock absorbers				66000		

Libreta Tributaria	No.	9007695	
Reg. de Timbres	No.	039750	
S. S. Empleado		164-18302	
Patente Comercial		642789	
Reg. Mayorista	No.	01-0168-7	

Sub - Total	S/.	—
D. L. 19620	S/.	—
TOTAL	S/.	66000

CANCELADO

ob King LIMA 10 DE 2 DE 19 83

11/66

American-made
iew shocks to replace the ones you broke.
Please send the check to me, made out to MO.
Thanks, al

Tiistainen retki suuntautui Porontimajoelle. Ennen matkan alkua kokoonnuttiin yhteen "käskynjakoa" varten ja annettiin ohjeita varusteista.

Kuusamon jäkälät kongressin aiheena

Pohjoismainen jäkäläkongressi on retkeillyt viikon alkupäivinä Kuusamossa. Oulangan biologista asemaa tukikohtanaan käyttävällä kurssilla on mukana nelisenkymmentä osanottajaa.

Maanantaina retkeiltiin Juumassa Jäkälävuoman maisemissa. Tiistaina retkeläiset samosivat Virkkulassa Porontimajokivarressa ja tänään keskiviikkona matka suuntautuu Kuusinkijoelle.

Kongressia varten on julkistunut uusittu sienilista Koillismaan alueelta. Tässä luettelossa on lajimäärä kasvanut ja käsittää nyt 2331 lajia.

— **Sähkön kokonaiskulutus** nousi toukokuussa runsaaseen kolmeen miljardiin kilowattituntiin. Kasvu edellisen vuoden toukokuuhun oli yli viisi prosenttia. Viimeisten 12 kuukauden aikana sähkön kokonaiskulutus on kasvanut vajaat kaksi miljardia kilowattituntia eli viisi prosenttia.

Toukokuussa sähköstä kolmannes tuotettiin vesivoimalla ja samanverran ydinvoimalla.

"Kansainvälisyyttä" Pohjoismaiden ulkopuolelta jäkäläkongressis edustaa taiwanilainen Ming Jou Lai. Hän on kotoisin Taipeista.

ENT-LABDANES, MANOYLOXIDE AND HELIPTEROL DERIVATIVES FROM CHRYSOCEPHALUM AMBIGUUM

C. ZDERO, F. BOHLMANN and R.M. KING*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, Germany; *Smithsonian Institution, Dept. of Botany, Washington DC 20560, U.S.A.

(Received)

Key Word Index - Chrysocephalum ambiguum; Compositae; diterpenes; ent-labdanes; ent-manoyloxide derivatives; monocyclic diterpenes.

Abstract - The aerial parts of Chrysocephalum ambiguum afforded in addition to two known diterpenes 28 new ones, 22 ent-labdanes, four ent-manoyloxide derivatives and two monocyclic diterpenes derived from helipterol. The structures were elucidated by high field ^{1}H NMR spectroscopy.

INTRODUCTION

The large genus Helichrysum (Compositae, tribe Gnaphaliinae [1]) is mainly distributed over South Africa and Australia. New taxonomic studies indicated that the Australian species all belong to other genera [1]. But even after removal of the Australian species from Helichrysum, the genus is still heterogeneous and poorly circumscribed from related groups [1]. In continuation of our chemical studies of Helichrysum species from Australia [2] we now have studied Chrysocephalum ambiguum (Turcz.) A. Anderb. (= Helichrysum apiculatum (Labill.) D. Don.) from the subtribe Angianthinae [1].

RESULTS AND DISCUSSION

The extract of the aerial parts of Ch. ambiguum afforded in addition to the ent-labdanes 1 [3] and 18 [4] 22 new ones (2 - 17, 19 - 23 and 28), four ent-manoyloxide derivatives (24 - 27) and the monocyclic diterpenes 29 and 31. The acids 2 - 17, 24, 25, 28 and 29 were isolated as their methyl ester.

The ^{1}H NMR spectrum of 2a (Table 1) was similar to that of 1a. Howver, an additional down field signal at δ 5.26 and an acetoxy methyl singlet at δ 2.03 indicated the presence of an acetoxy derivative of 1a. The positition of the latter followed from the allylic coupling of the double doublet at δ 5.26 with H-14. The ^{13}C NMR spectrum (Table 2) also supports the structure. The configuration at C-12 could not be determined.

The molecular formula of 3a ($C_{23}H_{36}O_4$) indicated the presence of an isomer of 2a. The ^1H NMR spectrum (Table 1) and also the ^{13}C NMR data (Table 2) clearly show that a 16-acetoxy derivatives of 1a was present. The ^1H NMR spectra of 4a and 5a (Table 1) indicated that also the corresponding 2-methyl butyrate and isobutyrate were isolated.

The molecular formula of 6a showed that it again was an isomer of 2a. The ^1H NMR spectrum (Table 1) and the ^{13}C NMR data (Table 2) required a 19-acetoxy derivative of 1a. A W-coupling of H-19' established the position of the acetoxy group and the configuration at C-4.

The ^1H NMR data of 7a (Table 1) showed that we were dealing with the desacetyl derivative of 6a while that of 8a (Table 1) only agreed with the presence of the 16,19-diacetoxy derivative of 1a. Accordingly, two pairs of methylene groups with geminal couplings were observed. The ^{13}C NMR data (Table 2) also agree with the structure. The ^1H NMR spectrum of 9a differed only in part from that of 8a (Table 1). Especially, a down field shift of H-12 and an up field shift of H-16 were observed indicating the presence of a 13E-double bond.

The ^1H NMR spectrum of 10a (Table 1) differed from that of 8a by the up field shift of H-19, obviously due to the presence of a free 19-hydroxy group. The ^1H NMR data of 11a (Table 1) agreed with a 6ß-hydroxy derivative of 1a. This follows from spin decoupling. Irradiation of the signal at δ 3.81 collapsed the signals at δ 1.09 d (H-5), 2.66 dd (H-7α) and 2.03 dd (H-7ß) to a singlet and doublets, respectively. As irradiation of the two latter signals sharpened the exomethylene proton signals the position of the hydroxy group and its configuration was settled.

The ^{1}H NMR spectra of 12a and 13a (Table 3) required the presence of a pair of 13E/Z isomers with a 2ß-hydroxy and a 16-acetoxy group. The couplings of H-2 indicated the ß-configuration of the hydroxy group and the chemical shift of H-16 indicated the stereochemistry of the Δ^{13}bond. The ^{13}C NMR data of 12a (Table 2) also agree with the structure.

The ^{1}H NMR (Table 3) and the ^{13}C NMR data (Table 2) of 14a clearly show that the 2-keto derivative of 3a was present as followed from the signals of H-1 and H-3. A negative Cotton-effect supports the presence of an ent-labdane. Together with the negative sign of optical rotation of all these diterpenes therefore most likely all are belonging to the ent-series.

The ^{1}H NMR data of 15a (Table 3) were close to those of 12a. However, the 16-acetoxy group was missing as a methyl doublet at δ 2.15 (H-16) was visible. The ^{1}H NMR spectrum of 16a (Table 3) indicated that a derivative of 12a was present. An up field shift of H-2 and a methoxy singlet at δ 3.35 clearly showed that the corresponding methyl ether was present. The ^{13}C NMR data are added in Table 2.

The ^{1}H NMR data of 17a (Table 3) were similar to those of 11a. However, the olefinic methyl signal was replaced by the typical signals of a 16-acetoxy derivative like 3a.

The ^{1}H NMR spectrum of 19 (Table 4) differed from that of 18 mainly by the additional low field signal at δ 3.88 which indicated a 2ß-hydroxy derivative of 18. The corresponding 2-keto derivative was isolated in addition to 18 from a Blepharispermum species [4].

The ^{1}H NMR spectrum of 20 (Table 4) differed from that of 18 mainly by the replacement of the pair of double doublets (H-16) by a broadened singlet at δ 5.98. In agreement with the molecular formula therefore a 16-hydroxy derivative of 18 was present. As none of the signals were doubled and also in the ^{13}C NMR spectrum (Table 2) no additional signal were observed only one of the two possible epimers was isolated. The configuration at C-16 could not be determined.

The ^{1}H NMR data of 21 (Table 4) clearly showed that we were dealing with the 19-acetoxy derivative of 18 while that of 22 (Table 4) indicated that also the 2ß-methoxy derivative was isolated.

The spectral data of 23 (Table 4) were in part similar to those of 20. However, an additional low field signal at δ 3.93 indicated the presence of the 2ß-hydroxy derivative of 20.

The ^{1}H NMR spectra of 24a and 25a (Table 5) were in part similar to those of manoyloxide and its 13-epimer. The presence of 19-acyloxy derivatives followed from the typical signal of H-19 while the succinyl group could be deduced from the four proton singlet at δ 2.62. The stereochemistry was established by NOED. In the case of 24a clear effects were observed between H-20, H-17 (8%) and H-19 (8%) as well as between H-17 and H-14 (10%) but not with H-16. The changed configuration of 25a followed from effects between H-17, H-20 (8%) and H-16 (8%).

The ^{1}H NMR spectra of 26 and 27 (Table 5) clearly showed that again ent-manoyloxide derivatives were present. The molecular formulae ($C_{20}H_{32}O_3$) agreed with acid derivatives of manoyloxide. This could be established by the ^{1}H NMR data which required

19-oic acid. The stereochemistry was determined by NOED [26: H-20 with H-17 (8%), H-16 with H-14 (7%); 27: H-20 with H-17 (8%), H-16 with H-17 (7%)]. The 4-epi derivative of 26 has been isolated from a Leyssera species [5]. The ^{1}H NMR spectra differ in the expected way.

The ^{1}H NMR spectrum of 28a (Table 5) differed from those of all the other labdanes. Comparison with the spectra of similar compounds showed that we were dealing with a 15-acetoxy-ent-labda-7,13E-diene which has a 2β-succinyloxy group. The relative position of the ester groups was deduced from the ms spectrum which showed a fragment formed by loss of the side chain with the acetoxy group followed by loss of the succinoyl group.

The ^{1}H and ^{13}C NMR spectra of 29a (Table 6) were similar to those of helipterol (30) [6], the 5-desacyl derivative of 29. Spin decoupling showed that the additional succinyloxy group has to be placed at C-5 as the low field double triplet at δ 6.03 was coupled with an olefinic proton (H-6) and a pair of double doublets which were due to H-4.

The ^{1}H NMR data of 31 (Experimental) again were similar to those of 30. However, the exomethylene proton signals (H-18) were replaced by a methyl singlet. The absence of a NOE between H-18 and H-17 established the relative configuration at C-10 and C-11. The presented absolute configuration for 29 and 31 is not established but perhaps likely from biogenetic considerations. The stereochemistry at C-3 could not be determined.

The new results on the chemistry of the genus Chrysocephalum show similarities with those of a previous study of a subspecies of Ch. ambiguum [2] where also a large variety of ent-labdanes

were isolated but all being manoyloxide derivatives. From other genera placed in the Waitzia group of the subtribe Angianthinae [1] Rutidosis [7], Waitzia [8] and Pogonolepis [9] also contains labdanes while from the polyphyletic genus Podolepis, -pyrones and lignanes were isolated [10]. Hyalosperma gave monocyclic diterpenes [6], Leptotryche [11] and Angianthus [12], sesquiterpene lactones and Calocephalus [9], beyerane derivatives and thiopenacetylenes also present in Bellida [unpubl.]. Labdanes are also present in Myriocephalus species [11] which are close to the Waitzia group [1], while Polycalymna stuartii (= Myriocephalus stuartii) gave beyerane derivatives [14].

Thus the chemistry of the Waitzia group only in part is homogeneous. But surely not enough species have been studied to get a clear picture especially as often the chemistry of a genus is not homogeneous too.

EXPERIMENTAL

The air dried aerial parts (2.3 kg) (collected in SW Australia in January 1989, voucher RMK 9730, deposited in the US National Herbarium) were extracted with MeOH-Et_2O-petrol, 1 : 1 : 1, at room temp. The defatted extract (MeOH, 20°) was separated as reported previously [14]. The CC frs were combined into three (1: EtOAc-petrol, 1 : 9; 2: EtOAc-petrol, 3 : 2 and 3: EtOAc). Fr 1 gave by TLC 300 mg fatty acids and 200 mg 1. Fr 2 contained a complex mixture of acids. As in the ^1H NMR no carbomethoxy signal was visible the whole mixture was esterified by addition of

excess CH_2N_2. Medium pressure chromatography (SiO_2, ⌀ 30 - 60) gave 10 frs (petrol, EtOAc-petrol, 1 : 9 - 3 : 1, EtOAc). Fr 2/1 gave by HPLC (MeOH-H_2O, 19 : 1, always RP 8, flow rate 3 ml/min) 1 g 2a (R_t 5.1 min), 50 mg 3a (R_t 6.5 min), 5 mg 5a (R_t 8.4 min) and 1.5 mg 4a (R_t 10.5 min). Fr 2/2 gave by HPLC (MeOH) 1 g 6a (R_t 1.9 min) and 1 g 3a (R_t 2.5 min). Fr 2/3 gave by HPLC (MeOH-H_2O, 19 : 1) 5 mg phytol and a mixture which gave by HPLC (MeOH-H_2O, 14 : 1) 150 mg 8a (R_t 5.8 min), 30 mg 24a (R_t 6.8 min), 4 mg 25a (purified by TLC (EtOAc-petrol, 1 : 9)) and a mixture which gave by TLC (Et_2O-petrol-MeOH, 20 : 180 : 1, two develloppments) 10 mg 9a (R_f 0.60) and 40 mg 11a (R_f 0.45). Fr 2/4 gave 1.2 g 8a and fr 2/5 by HPLC (MeOH-H_2O, 9 : 1) 16a (R_t 6.3 min), 30 mg 28a (R_t 8.0 min), 40 mg 18 (R_t 5.8 min) and two mixtures (2/5/1 and 2/5/2). Fr 2/5/1 gave by TLC (Et_2O-petrol, 1 : 3, 2 x) 2 mg 26 (R_f 0.55) and 5 mg 27 (R_f 0.50). Fr 2/5/2 afforded by TLC (Et_2O-petrol, 1 : 3, 2 x) 3 mg 7a (R_f 0.35). Fr 2/6 gave by HPLC (MeOH-H_2O, 9 : 1) 10 mg 14a (R_t 3.1 min), 30 mg 17a (R_t 3.5 min), 3 mg 31 (R_t 4.2 min), 30 mg 20 (R_t 5.0 min), 5 mg 29a (R_t 6.1 min) and a mixture which gave by TLC (Et_2O-petrol, 1 : 3) 30 mg 5,7,4'-trihydroxyflavanone and 10 mg geraniol. Fr 2/7 afforded by HPLC (MeOH-H_2O, 4 : 1) 10 mg 21 (R_t 3.9 min), 5 mg 13a (R_t 5.3 min), 150 mg 12a (R_t 5.8 min), 5 mg 15a (R_t 7.3 min) and a mixture which gave by TLC (Et_2O-petrol, 1 : 3) 5 mg 10a (R_f 0.50) and 5 mg 22 (R_f 0.38). Fr 2/8 gave 1.8 g 12a and fr 2/9 1.4 g 12a and 0.7 g 19. Fr 2/10 gave by HPLC (MeOH-H_2O, 4 : 1) 10 mg 23 (R_t 2.3 min) and 0.5 g 19. CC 3 contained 4 g 12a and 1 g 19. Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material.

12-Acetoxy-ent-labda-8(17),13E-dien-15-oic acid (2). Isolated as its methyl ester 2a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 885 (C=CH$_2$), 1745 (OAc), 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 376.261 [M]$^+$ (10) (calc. for $C_{23}H_{36}O_4$: 376.261), 316 [M - HOAc]$^+$ (88), 301 [316 - Me]$^+$ (24), 257 [317 - CO$_2$Me]$^+$ (22), 205 [$C_{15}H_{25}$]$^+$ (51), 137 (100), 95 (77), 81 (85), 55 (95).

16-Acetoxy-ent-labda-8(17),13Z-dien-15-oic acid (3). Isolated as its methyl ester 3a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3085, 890 (C=CH$_2$), 1745 (OAc), 1730, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 376.261 [M]$^+$ (18) (calc. for $C_{23}H_{36}O_4$: 376.261), 361 [M - Me]$^+$ (12), 316 [M - HOAc]$^+$ (85), 303 [M - CH$_2$OAc]$^+$ (64), 301 [316 - Me]$^+$ (78), 257 [316 - CO$_2$Me]$^+$ (28), 177 (62), 137 (100), 95 (88), 81 (88), 69 (90), 55 (82); $[\alpha]_D^{24°}$ +36 (CHCl$_3$; c 6.35).

16-[2-methylbutyryloxy]-ent-Labda-8(17),13Z-dien-15-oic acid (4). Isolated as its methyl ester 4a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO$_2$R), 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 418.308 [M]$^+$ (3) (calc. for $C_{26}H_{42}O_4$: 418.308), 403 [M - Me]$^+$ (2), 386 [M - MeOH]$^+$ (3.5), 316 [M - RCO$_2$H]$^+$ (100), 301 [316 - Me]$^+$ (48), 257 [316 - CO$_2$Me]$^+$ (17), 177 (24), 137 (78), 95 (50), 85 [RCO]$^+$ (44), 81 (60), 69 (74), 57 [85 - CO]$^+$ (100).

16-Isobutyryloxy-ent-labda-8(17),13Z-dien-15-oic acid (5). Isolated as its methyl ester 5a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3090, 905 (C=CH$_2$), 1740 (CO$_2$R), 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.):

404.293 [M]+ (8) (calc. for $C_{25}H_{40}O_4$: 404.293), 389 [404 - Me]+ (5), 373 [M - OMe]+ (6), 372 [M - MeOH]+ (6), 316 [M - RCO_2H]+ (100), 303 [M - CH_2OCOR]+ (42), 301 [316 - Me]+ (80), 257 [316 - CO_2Me]+ (25), 177 (42), 137 (92), 95 (73), 81 (80), 71 [RCO]+ (84).

19-Acetoxy-ent-labda-8(17),13E-dien-15-oic acid (6). Isolated as its methyl ester 6a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 890 ($C=CH_2$), 1750 (OAc), 1725, 1650 ($C=CCO_2R$); MS m/z (rel. int.): 376.261 [M]+ (35) (calc. for $C_{23}H_{36}O_4$: 376.261), 361 [M - Me]+ (20), 316 [M - HOAc]+ (37), 303 [M - CH_2OAc]+ (40), 203 (44), 135 (100), 107 (80), 81 (80), 55 (72); $[\alpha]_D^{24°}$ -27 ($CHCl_3$; c 3.15).

19-Hydroxy-ent-labda-8(17),13E-dien-15-oic acid (7). Isolated as its methyl ester 7a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640 (OH), 1725, 1650 ($C=CCO_2R$); MS m/z (rel. int.): 334.251 [M]+ (8) (calc. for $C_{21}H_{34}O_3$: 334.251), 303 [M - OMe]+ (41), 203 (22), 137 (51), 135 (50), 123 (73), 114 (100), 95 (82), 81 (86).

16,19-Diacetoxy-ent-labda-8(17),13Z-dien-15-oic acid (8). Isolated as its methyl ester 8a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 890 ($C=CH_2$), 1745 (OAc), 1725, 1650 ($C=CCO_2R$); MS m/z (rel. int.): 434.267 [M]+ (8) (calc. for $C_{25}H_{38}O_6$: 343.267), 374 [M - HOAc]+ (84), 361 [M - CH_2OAc]+ (60), 342 [374 - MeOH]+ (22), 314 [374 - HOAc]+ (45), 301 [374 - CH_2OAc]+ (55), 203 (42), 135 (100), 121 (72), 107 (80), 93 (78), 81 (80); $[\alpha]_D^{24°}$ -28 ($CHCl_3$; c 10.5).

16,19-Diacetoxy-ent-labda-8(17),13E-dien-15-oic acid (9). Isolated as its methyl ester 9a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (OAc), 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 434.267 [M]$^+$ (10) (calc. for $C_{25}H_{38}O_6$: 434.267), 374 [M - HOAc]$^+$ (66), 361 [M - CH_2OAc]$^+$ (66), 332 [374 - ketene]$^+$ (22), 314 [374 - HOAc]$^+$ (26), 301 [374 - CH_2OAc]$^+$ (48), 203 (52), 135 (100), 121 (88), 107 (86), 93 (80), 81 (83), 55 (80).

16-Acetoxy-19-hydroxy-ent-labda-8(17),13Z-dien-15-oic acid (10). Isolated as its methyl ester 10a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640 (OH), 1750 (OAc), 1725, 1645 (C=CCO$_2$R); MS m/z (rel. int.): 392.256 [M]$^+$ (7) (calc. for $C_{23}H_{36}O_5$: 392.256), 332 [M - HOAc]$^+$ (24), 319 [M - CH_2OAc]$^+$ (22), 301 [319 - H_2O]$^+$ (76), 203 (66), 135 (100), 98 (97), 81 (94).

6ß-Hydroxy-ent-labda-8(17),13E-dien-15-oic acid (11). Isolated as its methyl ester 11a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 3080, 890 (C=CH$_2$), 1725, 1655 (C=CCO$_2$R); MS m/z (rel. int.): 334.251 [M]$^+$ (14) (calc. for $C_{21}H_{34}O_3$: 334.251), 319 [M - Me]$^+$ (10), 316 [M - H_2O]$^+$ (14), 301 [316 - Me]$^+$ (10), 203 (25), 114 (100), 95 (36), 69 (70); $[\alpha]_D^{24°}$ -41 ($CHCl_3$; c 3.8).

2ß-Hydroxy-16-acetoxy-ent-labda-8(17),13Z-dien-15-oic aicd (12). Isolated as its methyl ester 12a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3090, 920 (C=CH$_2$), 1750 (OAc), 1720, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 374.246 [M]$^+$ (3.5) (calc. for $C_{23}H_{36}O_5$: 374.246), 359 [374 - Me]$^+$ (4), 314 [M - HOAc]$^+$ (15), 299 [314 - Me]$^+$ (21), 203 (23), 135 (100).

16-Acetoxy-2ß-hydroxy-ent-labda-8(17),13E-dien-15-oic acid (13). Isolated as its methyl ester 13a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1750 (OAc), 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 392.256 [M]$^+$ (3) (calc. for $C_{23}H_{36}O_5$: 392.256), 374 [M - H_2O]$^+$ (21), 359 [374 - Me]$^+$ (23), 332 [M - HOAc]$^+$ (22), 314 [332 - H_2O]$^+$ (67), 301 [374 - CH_2OAc]$^+$ (30), 299 [314 - Me]$^+$ (35), 231 (50), 203 (81), 135 (100), 95 (80), 81 (82), 69 (86).

16-Acetoxy-2-oxo-ent-labda-8(17),13Z-dien-15-oic acid (14). Isolated as its methyl ester 14a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750 (OAc), 1725, 1650 (C=CCO$_2$R), 1725 (C=O), 3090, 910 (C=CH$_2$); MS m/z (rel. int.): 390.241 [M]$^+$ (2) (calc. for $C_{23}H_{34}O_5$: 390.241), 375 [M - Me]$^+$ (5), 358 [M - MeOH]$^+$ (2.5), 330 [M - HOAc]$^+$ (17), 317 [M - CH_2OAc]$^+$ (24), 298 [358 - HOAc]$^+$ (35), 231 (22), 151 (100), 112 (52), 81 (42); CD (MeOH): $\Delta\varepsilon_{287}$ -0.31.

2ß-Hydroxy-ent-labda-8(17),13E-dien-15-oic acid (15). Isolated as its methyl ester 15a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 3090, 910 (C=CH$_2$); 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 334.251 [M]$^+$ (11) (calc. for $C_{21}H_{34}O_3$: 334.251), 319 [M - Me]$^+$ (17), 316 [M - H_2O]$^+$ (30), 301 [316 - Me]$^+$ (66), 203 (66), 135 (100), 114 (88), 95 (73), 81 (78).

2ß-Methoxy-16-acetoxy-ent-labda-8(17),13Z-dien-15-oic acid (16). Isolated as its methyl ester 16a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3085, 905 (C=CH$_2$), 1750 (OAc), 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 406.272 [M]$^+$ (3) (calc. for $C_{24}H_{38}O_5$: 406.272), 391 [M - Me]$^+$ (5), 374 [M - MeOH]$^+$ (21), 346 [374 - CO]$^+$ (20), 314 [374 - HOAc]$^+$ (72), 299 [314 - Me]+ (43), 203 (61), 135 (100), 81 (60).

6ß-Hydroxy-16-acetoxy-ent-labda-8(17),13Z-dien-15-oic acid (17). Isolated as its methyl ester 17a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620 (OH), 1755 (OAc), 1730, 1650 (C=CCO$_2$R), 3090, 920 (C=CH$_2$); MS m/z (rel. int.): 374.246 [M - H$_2$O]$^+$ (5) (calc. for $C_{23}H_{34}O_4$: 374.246), 359 [374 - Me]$^+$ (4), 314 [374 - HOAc]$^+$ (44), 301 [374 - CH$_2$OAc]$^+$ (22), 299 [314 - Me]$^+$ (20), 203 (38), 135 (57), 112 (96), 81 (60), 69 (100); $[\alpha]_D^{24°}$ -25 ($CHCl_3$; c 2.73).

2ß-Hydroxy-ent-labda-8(17),13-dien-15,16-olide (19). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1750 (γ-lactone); MS m/z (rel. int.): 318.219 [M]$^+$ (1) (calc. for $C_{20}H_{30}O_3$: 318.219), 300 [M - H$_2$O]$^+$ (20), 285 [300 - Me]$^+$ (30), 203 (47), 135 (90), 98 (100).

16-Hydroxy-ent-labda-8(17),13-dien-15,16-olide (20). Crystals, mp. 119°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380 (OH), 1755 (γ-lactone); MS m/z (rel. int.): 318.219 [M]$^+$ (5) (calc. for $C_{20}H_{30}O_3$: 318.219), 303 [M - Me]$^+$ (7), 300 [M - H$_2$O]$^+$ (7), 290 [M - CO]$^+$ (6.5), 285 [300 - Me]$^+$ (6), 203 (11), 177 (20), 137 (100), 123 (55), 81 (44); $[\alpha]_D^{24°}$ -100 ($CHCl_3$; c 0.43).

19-Acetoxy-ent-labda-8(17),13-dien-15,16-olide (21). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1775 (γ-lactone), 1745 (OAc); MS m/z (rel. int.): 360.230 [M]$^+$ (4) (calc. for $C_{22}H_{32}O_4$: 360.230), 342 [M - H$_2$O]$^+$ (4), 300 [M - HOAc]$^+$ (68), 203 (94), 135 (88), 109 (100), 95 (91), 81 (91).

2ß-Methoxy-ent-labda-8(17),13-dien-15,16-olide (22).
IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 (γ-lactone); MS m/z (rel. int.): 332.235 $[M]^+$ (8) (calc. for $C_{21}H_{32}O_3$: 332.235), 317 $[M - Me]^+$ (10), 300 $[M - MeOH]^+$ (52), 285 $[300 - Me]^+$ (44), 218 (28), 213 (68), 175 (33), 135 (100), 111 (90), 98 (87).

2ß,16-Dihydroxy-ent-labda-8(17),13-dien-15,16-olide (23).
IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone); MS m/z (rel. int.): 334 $[M]^+$ (1), 316.204 $[M - H_2O]^+$ (10) (calc. for $C_{20}H_{28}O_3$: 316.204), 301 $[316 - Me]^+$ (8), 203 (20), 135 (100), 121 (38), 69 (40).

19-Succinyloxy-ent-manoyloxide (24). Isolated as its methyl ester 24a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 900 ($C=CH_2$), 1740 (CO_2R); MS m/z (rel. int.): 420.288 $[M]^+$ (4) (calc. for $C_{25}H_{40}O_5$: 420.288), 405 $[M - Me]^+$ (100), 273 $[405 - RCO_2H]^+$ (55), 255 (60), 190 (67), 115 $[RCO]^+$ (75), 95 (63), 81 (70).

19-Succinyloxy-13-epi-ent-manoyloxide (25). Isolated as its methyl ester 25a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 900 ($C=CH_2$), 1740 (CO_2R); MS m/z (rel. int.): 420.288 $[M]^+$ (3) (calc. for $C_{25}H_{40}O_5$: 420.288), 405 $[M - Me]^+$ (100), 374 $[405 - OMe]^+$ (6), 273 $[405 - RCO_2H]^+$ (51), 255 (66), 190 (70), 135 (66), 115 $[RCO]^+$ (83), 95 (60), 81 (71), 55 (78); $[\alpha]_D^{24°}$ -21 ($CHCl_3$; c 2.25).

13-epi-ent-Manoyloxide-19-oic acid (26, not free from 25). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 - 2600, 1700 (CO_2H), 3080, 1645, 930 ($C=CH_2$); MS m/z (rel. int.): 320.235 $[M]^+$ (3) (calc. for $C_{20}H_{32}O_3$: 320.235), 305 $[M - Me]^+$ (100), 287 (75), 222 (72), 81 (74), 55 (57).

ent-Manoyloxide-19-oic acid (27). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3300 - 2600, 1700 (CO_2H), 3080, 1645, 925 ($C=CH_2$); MS m/z (rel. int.): 320.235 $[M]^+$ (3) (calc. for $C_{20}H_{32}O_3$: 320.235), 305 $[M - Me]^+$ (100), 287 $[305 - H_2O]^+$ (85), 222 (81), 177 (46), 81 (73).

28-Succinyloxy-15-acetoxy-ent-labda-7,13E-diene (28). Isolated as its methyl ester 28a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (CO_2R, OAc); MS m/z (rel. int.): 462.298 $[M]^+$ (2) (calc. for $C_{27}H_{42}O_6$: 462.298), 334 $[M - Me_2C=CHCH_2OAc]^+$ (100), 202 $[334 - RCO_2H]^+$ (56), 115 $[RCO]^+$ (37), 81 (46).

5-Succinyloxyhelipterol (29). Isolated as its methyl ester 29a; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1745 (CO_2R), 3080, 1645, 910 ($C=CH_2$); MS m/z (rel. int.): 374.282 $[M - HCO_2Me]^+$ (0.3) (calc. for $C_{24}H_{38}O_3$: 374.282), 302 $[M - RCO_2H]^+$ (2), 270 (6), 255 (5), 218 (20), 203 (37), 115 $[RCO]^+$ (81), 71 $[H_2C=CHC(OH)Me]^+$ (100).

11α-Hydroxy-11,18-dihydrohelipterol (31). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 3090, 930 ($CH=CH_2$); MS m/z (rel. int.): 290.261 $[M - H_2O]^+$ (7) (calc. for $C_{20}H_{34}O$: 290.261), 272 $[290 - H_2O]^+$ (5), 203 $[272 - C_5H_9]^+$ (21), 135 (46), 109 (77), 81 (94), 71 (62), 55 (100); ^1H NMR ($CDCl_3$): δ 0.68 (s, H-16), 0.96 (s, H-17), 1.17 (s,

H-18), 1.28 (s, H-20), 1.63 (br s, H-19), 2.02 (m, H-8, H-10, H-12), 5.07 (dd, H-1c), 5.15 (br t, H-6), 5.22 (dd, H-1t), 5.92 (dd, H-2); J [Hz]: 1c,1t = 1; 1c,2 = 11; 1t,2 = 17.

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Table 1. ^{1}H NMR spectral data of compounds 2a - 11a (400 MHz, $CDCl_3$, δ-values)

H	2a	3a	4a*	5a+	6a	7a	8a	9a	10a	11a
1α	1.66 br d	1.53 m	1.50 m	1.50 m	+	+	+	+	+	1.68 m
1ß	0.92 dt	0.98 dt	0.99 dt	0.98 dt	1.02 dt	1.05 dt	1.02 dt	1.00 dt	+	1.00 dt
2	+	1.49 m	1.50 m	1.50 m	+	+	+	+	+	+
2'	+	+	+	+	+	+	+	+	+	+
3α	1.37 br d	1.37 br d	1.39 br d	1.39 br d	+	+	+	1.50 m	+	1.36 br d
3ß	1.16 dt	1.15 dt	1.15 m	1.18 dt	1.26 dt	+	+	1.28 m	+	1.22 dt
5	1.04 dd	1.06 dd	1.08 dd	1.08 dd	1.28 dd	+	1.24 dd	1.26 dd	1.25 dd	1.09 d
6α	1.28 dq	1.30 dq	1.31 dq	1.30 dq	1.35 dq	1.32 dq	1.34 dq	1.35 dq	1.32 dq	3.81 br dt
6ß	1.70 m	1.72 dt	1.73 br d	1.72 br d	1.75 m	1.75 m	1.71 br d	1.74 m	1.76 br d	-
7α	2.35 ddd	2.37 ddd	2.39 m	2.38 br d	2.38 ddd	2.39 m	2.39 m	2.39 br d	2.39 br d	2.66 dd
7ß	1.87 br dt	1.96 br dt	1.98 m	2.00 m	1.95 br dt	1.95 m	1.95 m	1.96 m	1.95 m	2.03 dd
9	1.78 m	1.58 br d	1.58 br d	1.58 br d	1.57 br d	1.57 br d	1.59 br d	1.56 m	1.60 br d	1.59 br d
11		1.49 m	1.49 m	1.50 m	1.50 m	1.50 m	1.49 m	1.50 m	1.50 m	1.47 m
12	5.26 dd	2.39 br dt	2.39 m	2.40 br dt	2.27 br dt	2.29 br dt	2.39 m	2.57 br dt	2.42 m	2.28 br dt
12'		1.96 m	1.98 m	1.95 br dt	1.95 m	1.96 m	1.95 m	1.96 m	1.95 m	1.97 m
14	5.76 br s	5.76 dq	5.77 dq	5.77 dq	5.63 tq	5.65 tq	5.75 tt	5.83 tt	5.77 tt	5.63 tq
16	2.11 d	5.29 dd 5.12 dd	5.28 dd 5.18 dd	5.28 dd 5.17 dd	2.14 d	2.15 d	5.29 dd 5.12 dd	4.59 br s	5.31 dd 5.14 dd	2.14 d
17	4.89 q	4.83 q	4.83 q	4.83 q	4.84 q	4.84 q	4.84 q	4.88 q	4.84 q	4.90 q
17'	4.74 q	4.49 q	4.48 q	4.48 q	4.50 q	4.50 q	4.50 q	4.67 q	4.51 q	4.55 q
18	0.86 s	0.86 s	0.86 s	0.87 s	0.95 s	0.98 s	0.95 s	0.95 s	0.97 s	1.16 s
19	0.78 s	0.78 s	0.80 s	0.80 s	4.20 d 3.83 dd	3.73 d 3.39 dd	3.83 d 3.70 d	4.20 d 3.83 d	3.74 d 3.39 dd	0.99 d
20	0.67 s	0.66 s	0.67 s	0.67 s	0.67 s	0.65 s	0.67 s	0.67 s	0.65 s	0.68 s
OAc	2.03	2.07 s	-	-	2.02 s	-	2.07 s	2.02 s	2.08 s	
							2.02 s	2.12 s		
CO_2Me	3.96 s	3.96 s	3.70 s	3.70 s	3.68 s	3.69 s	3.70 s	3.70 s	3.70 s	3.67 s

*) OMebu 2.39 tq, 1.67 m, 1.49 m, 0.91 t, 1.16 d; $^{+}$) 2.58 qq, 1.18 d; $^{+}$) overlapped multiplets.

J [Hz]: 1α,1ß = 1ß,2α = 2α,3ß = 3α,3ß ~ 12; 5,6α = 6α,6ß = 6α,7ß = 13; 5,6ß = 2.5; 6α,7α = 3; 6ß,7ß = 2; 7α,7ß = 13; 9,11 = 11; 11,12 = 11',12' = 12,12' ~ 12; 11',12 = 11,12' ~ 4; 12,14 = 14,16 ~ 1 (compound 2a: 11,12 = 7; 11',12 = 9; compounds 3a - 5a, 8a and 10a: 16,16' = 15; compounds 6a - 10a: 3ß,19 ~ 1; 19,19' = 11; compound 11a: 5,6α = 6α,6ß = 6α,7ß = 12; 6α,7α = 4).

Table 2. ^{13}C NMR spectral data of compounds 2a, 6a, 8a, 12a, 14a and 20a (100.6 MHz, $CDCl_3$, δ-values)*

C	2a	3a	6a	8a	12a	14a	16a	20a
1	41.9	42.0	39.5	38.7	50.8	56.1	47.1	42.0
2	19.3	19.3	18.8	18.7	65.3	211.1	74.3	19.3
3	39.8	39.0	38.7	38.3	48.0	53.9	44.5	39.7
4	33.5	33.5	39.4	37.1	34.9	38.9	34.6	33.6
5	55.3	56.4	56.0	56.2	56.2	55.8	56.4	56.3
6	24.3	24.4	24.3	24.3	23.8	24.3	23.9	24.3
7	38.1	33.9	36.0	33.7	33.8	33.4	33.9	38.2
8	147.5	148.2	147.4	147.2	147.2	146.4	147.3	147.8
9	52.3	55.4	55.9	56.0	54.7	54.7	55.6	55.4
10	39.4	39.7	37.2	39.4	41.0	44.8	40.7	39.7
11	26.7	22.0	21.4	21.9	22.1	22.1	22.6	20.8
12	78.2	38.2	38.3	36.0	37.8	37.5	37.9	26.7
13	155.2	157.5	160.8	157.2	157.2	156.7	157.2	170.4
14	118.2	117.3	114.9	117.2	117.3	117.6	117.3	117.0
15	166.7	166.2	167.2	165.9	166.0	166.0	166.1	171.6
16	14.5	62.6	18.7	62.4	62.5	62.5	62.5	99.1
17	107.4	109.3	106.7	106.7	107.1	107.7	107.0	106.5
18	33.4	33.5	27.4	27.4	33.5	33.3	33.9	33.6
19	21.7	21.7	66.6	66.4	22.5	23.0	22.6	21.7
20	13.8	14.4	15.1	15.1	15.2	15.2	15.3	14.4
OAc	170.0	170.5	171.2	171.0	170.5	170.4	170.6	-
	21.2	20.8	20.9	170.2	20.8	20.7	20.7	-
				20.8				
				20.6				
OMe	51.1	51.2	50.7	51.1	51.2	51.3	51.2	-
							55.0	-

*) Some signals may be interchangeable.

Table 3. ^{1}H NMR spectral data of compounds 12a - 17a (400 MHz, $CDCl_3$, δ-values)

H	12a(C_6D_6)	13a	14a$^+$	15a	16a	17a
2	3.67 tt	3.86 tt	-	3.88 tt	3.36 tt	*
5	0.85 dd	1.09 dd	1.66 dd	1.07 dd	1.08 dd	1.11 d
6α	1.19 dq	1.29 dq	1.41 dq	1.29 dq	1.30 dq	3.88 dt
6β	1.57 br d	1.77 br d	2.02 m	1.77 br d	1.84 br d	-
7α	2.34 ddd	2.41 ddd	2.46 ddd	2.40 ddd	2.40 br d	2.67 dd
7β	1.87 br dt	1.98 br dt	2.02 m	1.96 m	1.97 m	2.00 m
9	1.52 br d	1.73 br d	*	1.63 br d	1.65 br d	1.62 br d
12	2.43 ddd	2.62 ddd	2.40 m	2.29 dt	2.40 m	2.41 m
12'	1.98 ddd	2.45 ddd	2.02 m	1.96 m	1.97 m	2.00 m
14	5.93 tt	5.83 tt	5.75 tt	5.64 br s	5.77 tt	5.77 tt
16	5.67 dd	4.63 dd	5.29 dd	2.15 d	5.29 dd	5.29 dd
16'	5.51 dd	4.58 dd	5.13 dd		5.15 dd	5.13 dd
17	4.93 q	4.92 q	4.94 q	4.88 q	4.88 q	4.91 q
17'	4.60 q	4.70 q	4.58 q	4.53 q	4.53 q	4.57 q
18	0.85 s	0.94 s	1.06 s	0.93 s	0.94 s	1.16 s
19	0.76 s	0.84 s	0.84 s	0.84 s	0.84 s	1.00 s
20	0.65 s	0.71 s	0.70 s	0.72 s	0.72 s	0.68 s
OAc	1.76 s	2.13 s	2.07 s	-	2.08 s	2.08 s
OMe	3.42 s	3.70 s	3.71 s	3.68 s	3.70 s	3.70 s
					3.35 s	

*) Overlapped multiplets; $^+$) H-1 2.17 dd, 2.32 br d, H-3 2.40 dd, 2.15 br d.

J [Hz]: 1α,2 = 2,3α = 3.5; 1β,2 = 2,3β = 1α,1β = 3α,3β = 12; 5,6α = 6α,6β = 6α,7β = 13; 5,6β = 2.5; 6β,7α = 2; 6β,7β = 3; 7α,7β = 13; 9,11 = 11; 11,12 = 11',12' = 12,12' ~ 12; 11,12' = 11',12 ~ 4; 12,14 = 14,16 ~ 1; 16,16' = 15 (compound 17a: 5,6α = 6α,7β = 11; 6α,7α = 4).

Table 4. ^{1}H NMR spectral data of compounds 19 - 23 (400 MHz, $CDCl_3$, δ-values)

H	19	20	21	21$^+$	23
1α	2.07 br d	*	*	2.11 br d	2.10 br d
1β	0.96 t	*	*	0.94 t	0.98 t
2	3.88 tt	*	*	3.37 tt	3.93 tt
3α	1.77 br d	*	*	1.76 br d	1.75 m
3β	1.15 t	*	*	1.07 t	1.17 t
5	1.07 dd	1.09 dd	1.26 dd	1.11 dd	1.09 dd
6α	1.30 dq	1.33 dq	1.37 dq	1.31 dq	1.31 dq
6β	1.67 m	*	1.78 m	1.87 br d	*
7α	2.41 dd	2.40 ddd	2.42 ddd	2.42 ddd	2.42 br d
7β	1.95 dt	1.96 dt	1.92 m	1.97 dt	1.97 m
12	2.54 m	*	2.53 m	2.55 m	2.40 m
12'	2.25 m	*	2.27 m	2.25 m	1.97 m
14	5.83 tt	5.84 dt	5.85 tt	5.84 tt	5.86 dt
16	4.74 dd	5.98 br s	4.75 dd	4.75 dd	6.01 br s
16'	4.68		4.69 dd	4.70 dd	
17	4.91 q	4.85 q	4.89 q	4.92 q	4.91 q
17'	4.47 q	4.63 q	4.47 q	4.49 q	4.52 q
18	0.93 s	0.88 s	0.97 s	0.95 s	0.95 s
19	0.84 s	0.80 s	4.21 d 3.85 dd	0.85 s	0.85 s
20	0.73 s	0.70 s	0.71 s	0.74 s	0.74 s
OAc	-	-	2.04 s	-	-

*) Overlapped multiplets; $^+$) OMe 3.36 s.

J [Hz]: 1α,2 = 2,3α = 3.5; 1β,2 = 2,3β = 1α,1β = 3α,3β = 12; 5,6α = 6α,6β = 6α,7β = 13; 5,6β = 2.5; 6β,7α = 2; 6β,7β = 3; 7α,7β = 13; 12,14 = 12',14 = 14,16 ~ 1; 14,16 = 1.5; 16,16' = 18 (compound 21: 19,19' = 11; 3β,19' ~ 1).

Table 5. ^{1}H NMR spectral data of compounds 24a, 25a, 26, 17 and 28a (400 MHz, $CDCl_3$, δ-values)

H	24a	25a	26	27	28a*
14	5.99 dd	5.85 dd	6.01 dd	5.87 dd	5.35 br t
15c	4.90 d	4.91 d	4.92 dd	4.93 dd	} 4.59 d
15t	4.95 d	5.13 dd	4.97 d	5.15 dd	
16	1.11 s	1.12 s	1.31 s	1.13 s	1.71 br s
17	1.19 s	1.26 s	1.27 s	1.23 s	1.69 br s
18	0.93 s	0.93 s	1.23 s	1.23 s	0.96 s
19	{ 4.20 d 3.87 dd	{ 4.22 d 3.84 dd	-	-	0.92 s
20	0.72 s	0.79 s	0.65 s	0.72 s	0.84 s
OMe	3.68 s	3.68 s	-	-	3.70 s
OCOR	2.62 br s	2.62 br s	-	-	2.62 br s

*) H-7 5.40 br s, H-2 5.02 tt.

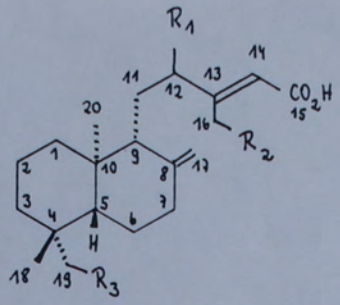
J [Hz]: Compounds 24a, 25a, 26 and 27: 14,15c = 10.5; 14,15t = 17; 15c,15t ~ 1 (compounds 24a and 25a: 3,19' = 1; 19,19' = 11); compound 28a: 1,2 = 2,3 = 12; 1',2 = 2,3' = 3.7; 14,15c = 11; 14,15t = 17; 15c,15t = 1.

Table 6. NMR spectral data of compounds 29a and 30 (400 and 100.6 MHz, $CDCl_3$, δ-values)

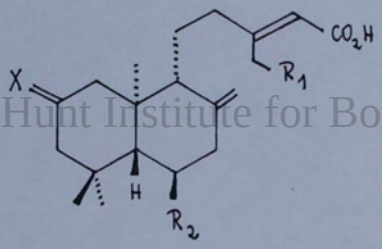
C	29a	30
1	111.6	111.7
2	144.7	145.1
3	72.0	73.5
4	47.1	42.1
5	69.6	22.7
6	124.2	123.8
7	140.1	136.2
8	32.2	32.8
9	24.3	24.7
10	53.5	53.6
11	148.9	149.3
12	36.0	36.3
13	23.6	23.7
14	38.0	38.2
15	34.6	34.9
16	28.1	27.9
17	26.1	26.2
18	109.2	108.8
19	16.7	16.1
20	28.5	28.4
OCOR	1.71 0	-
	29.2	
	28.7	
	172.0	
	50.9	

H	29a(C_6D_6)
1c	5.08 dd
1t	5.46 dd
2	5.87 dd
4	2.13 dd
4'	1.74 dd
5	6.03 ddd
6	5.36 br d
10	1.68 dd
16	0.86 s
17	0.98 s
18	4.89 dd
18'	4.70 d
19	1.85 br s
20	1.28 s
OCOR	2.25 m
OMe	3.32 s

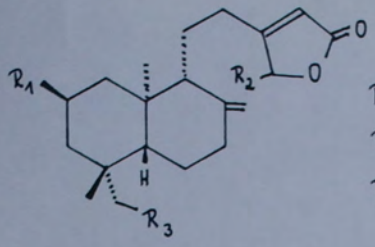
J [Hz]: 1c,1t = 1.5; 1c,2 = 10.5; 1t,2 = 17; 4,4' = 14; 4,5 = 8; 4',5 = 3.5; 5,6 = 9; 9,10 = 11; 9',10 = 3; 12,18 = 2; 9',18' = 12',18' ~ 1.5.



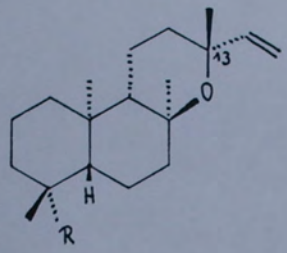
	1	2	3	4	5	6	7	8	9	10
R_1	H	OAc	H	H	H	H	H	H	H	H
R_2	H	H	OAc	OMebu	OiBu	H	H	OAc	OAc	OAc
R_3	H	H	H	H	H	OAc	OH	OAc	OAc 13E	OH

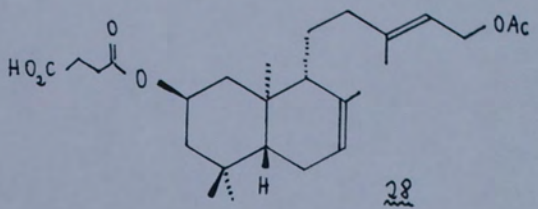


	11	12	13	14	15	16	17
R_1	H	OAc	OAc	OAc	H	OAc	OAc
R_2	OH	H	H	H	H	H	OH
X	H_2	βOH,H	βOH,H 13E	=O	βOH,H	βOMe,H	H_2



	18	19	20	21	22	23
R_1	H	OH	H	H	OMe	OH
R_2	H	H	OH	H	H	OH
R_3	H	H	H	OAc	H	H





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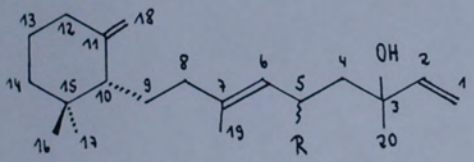
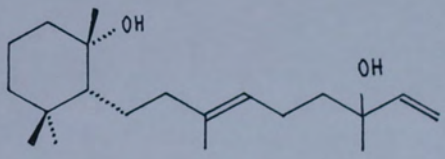
	24	25	26	27
R	CH_2O Succ		CO_2H	CO_2H
	13 epi			13 epi



29 R = 

30 R = H



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1a - 17a, 24a, 25a, 28a and 29a are the corresponding methylester

ENT-PIMARENE DERIVATIVES FROM PALAFOXIA ARIDA

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Key Word Index - Palafoxia arida, P. texana var. ambigua; Compositae; diterpenes; ent-pimarenes; glycosides; manoyloxide derivative, geranyl caprylate.

Abstract - The aerial parts of Palafoxia arida gave in addition to a known ent-pimarene derivative ten further ones, a manoyl oxide derivative and a new geranyl ester. From P. texana var. ambigua three known E-biformene derivatives were isolated. The structures were elucidated by high field NMR spectroscopy and the chemo- taxonomy of the difficult genus Palafoxia is discussed briefly.

INTRODUCTION

Palafoxia is a genus which is distributed over the South Eastern part of the United States and Mexico. Traditionally it was placed in the tribe Helenieae near Bahia and Chaenactis [1]. As, however, this tribe has been dismembered the position this genus is in question. The first proposal was the placement of Palafoxia in a subtribe of Eupatorieae [2]. Later it has been transferred to the Heliantheae in the subtribe Chaenactidinae [3]. So far chemical investigations have shown that pimarane and rosane derivatives are present in three of the 11 species [4 - 8]. P. rosea also gave labdanes and manoyloxide derivatives [6,9,10]. From P. arida B.L. Turner et M.I. Morris [11] collected in Arizona daturigenol, a pimarene derivative, is reported [4]. We now have studied again a sample of this species from California. The results are discussed in this paper.

RESULTS AND DISCUSSION

The extract of the aerial parts of Palafoxia arida afforded α-humulene, geranyl caprylate 16, methyl linolenoate and a complex mixture of diterpenes, most of them only could be separated after acetylation. Finally the ent-pimarane derivatives 1 [7], 3 and 2Ac - 11Ac as well as the ent-manoyloxide derivative 12 were isolated.

The structure of the ester 16 easily could be deduced from its ^{1}H NMR and MS spectrum. The latter indicated that a caprylate of geraniol must be present. The triol 1 is the main constituent, it is the Δ^7isomer of daturigenol, the only diterpene isolated previously from this species [4].

The ^1H NMR spectrum of 2Ac (Table 1) was close to that of 1Ac. However, the couplings of H-3 showed that 2Ac was the 3α-epimer of 1Ac. Accordingly, alanate reduction of 6Ac and acetylation (s. below) afforded a triacetate which was identical with 2Ac.

The ^1H NMR spectrum of 3 and its triacetate 3Ac (Table 1) indicated that again a pimarene was present. Triplets of triplets at δ 3.86 and 4.96 respectively showed that 3 was a regio-isomer of 1 with an equatorial hydroxy group at C-2 as followed from the vicinal couplings. The ^{13}C NMR spectrum (Experimental) also agrees with the structure.

The ^1H NMR spectrum of 4Ac (Table 1) indicated that this compound was the 18-acetoxy derivative of 3Ac. As already followed from the chemical shifts an equatorial acetoxy methylene group was present. This and the complete stereochemistry was established by the observed NOE's. Especially, the effects between H-17, H-14 (4%), H-14' (4%) and H-16 (5%), between H-20, H-2 (6%) and H-15 (3%) as well as between H-19, H-2 (6%) and H-18 (4%) required the proposed configuration of all chiral centers which agrees with that of daturigenol. However, the presence of two H-14 signals excluded a 8,14-double bond.

The ^1H NMR data of 5Ac (Table 1) clearly showed that this tetraacetate was the 18-acetoxy derivative of 1Ac. The presence of an axial oxygen function at C-3 followed from the small vicinal couplings and the position of equatorial orientation of the methylene acetoxy group at C-4 from the chemical shifts of H-18 which clearly differ in the corresponding compounds with oxygen functions at C-19.

The spectral data of 6Ac (Table 1) differed from those of 1Ac in the signals of the A-ring. Especially the absence of the low field signal around δ 5.0 and a pair of threefold doublets at δ 2.69 and 2.23 indicated that 6Ac was the corresponding 3-keto derivative. Alanate reduction gave a single triol (2) which after acetylation afforded 2Ac, identical with the triacetate obtained from the natural product.

The ^{1}H NMR spectrum of the triacetate 7Ac (Table 1) again showed the presence of a pimarene derivative with acetoxy groups at C-15, C-16 and C-18. A pair of downfield shifted signals were similar to those of 6Ac indicating again the presence of a keto group. The observed downfield shift of the H-18 signals showed that the keto group was at C-3. Furthermore, the observed positive Cotton effect indicated the presence of an ent-pimarene derivative. Accordingly, most likely all diterpenes from this species belong to the ent-series.

The ^{1}H NMR spectral data of 8Ac (Table 2) showed the presence of an acetylated ß-glucopyranoside as followed from spin decoupling. The chemical shifts required that this unit was at C-16 while a keto group again was at C-3. Accordingly, the signals were in part similar to those of 7Ac. Again a positive Cotton effect was observed which supports the proposed absolute configuration of the diterpenes. As followed from the ^{1}H NMR spectra (Table 2) the compounds 9Ac - 11Ac also were peracetylated ß-glucopyranosides differing only in the position of the oxygen functions in the diterpene part.

The major glycoside 9 was transformed by mild acetylation to the tetraacetate 9bAc and the pentaacetate 9aAc and by more

forced conditions to the hexaacetate 9Ac. All data indicated that the natural compound was a 16-O-ß-glucopyranoside of 3α,15,16-trihydroxy-ent-pimar-7-ene.

The ^{1}H NMR spectrum of 10Ac (Table 2) showed that the peracetylated 16-O-ß-glucopyranoside of 3 was present. Accordingly, the spectrum was in part very similar to that of 3Ac. The spectral data of 11Ac were close to those of 5Ac except the signals of the glucopyranoside part which were nearly identical with those of 9Ac and 10Ac.

The mass spectra of the glycosides always showed no molecular ions. However, the M - HOAc fragments mostly were relatively strong. As in similar cases the main fragments were due to the sugar moiety with m/z 169 as base peak (sugar part - 2 x HOAc and ketene).

The structure of the diterpene 12 also could be deduced from its ^{1}H NMR spectrum (Table 2) which clearly differed from those of 1 - 11 and their acetates respectively. Comparison of the spectrum with those of other diterpenes indicated that most likely a manoyl oxide derivative was present. The observed lowfield signals showed that the latter must have four further oxygen functions, three being hydroxyls and one an acetoxy group. The position of these functions and also the stereochemistry could be established by NOE difference spectroscopy. Thus effects were observed between H-20, H-17 (6%) and H-19 (6%), between H-17, H-15 (5%), H-19 (4%) and H-20 (7%) as well as between H-15 and H-17 (5%). Accordingly, H-15, H-17, H-19 and H-20 were all axial orientated on the same side of the molecule. The ^{13}C NMR (Experimental) also agrees with the structure. Furthermore,

acetylation of 12 gave the tetraacetate 12Ac not in agreement with a cyclic ether which could not be excluded as the highest peak in the MS of 12 was M - H_2O. The ^1H NMR data (Table 2) also supports the proposed structure. Though the absolute configuration could not be determined the proposed one is very likely as both types, the pimarenes and the manoyloxide surely have the same ent-labdane precursor.

This investigation again shows that ent-pimaranes are characteristic for the genus Palafoxia. However, precursors like 13 - 15 as well as ent-manoyloxide derivatives also are common. The rosanes, which are closely related to the pimaranes, are present in two species. The placement of Palafoxia in the subtribe Chaenactidinae [3] is supported by the chemistry of Hymenothrix [12], which is placed in the same subtribe, as it also contains rosanes. But, as the species of the other genera of the subtribe, Hymenothrix wislizenii also contains sesquiterpene lactones not reported from any Palafoxia species. Similar diterpenes are isolated from genera of the tribe Eupatorieae (Trichogonia [13], Kyrsteniopsis [14], Liatris [15] and Piqueria [16]) but also from Siegesbeckia [17] and Milleria [18] typical genera of the tribe Heliantheae. Accordingly, the placement of Palafoxia can not be decided only by the chemistry.

EXPERIMENTAL

The air dried aerial parts (550 g, collected in March 1989 in California, voucher RMK 9797, deposited in the US National Herbarium, Washington, U.S.A.) were extracted with MeOH-Et_2O-petrol, 1 : 1 : 1. The extract obtained was defatted with MeOH

and separated as reported previously [19]. Fractions of CC were combined to four portions (I - IV). TLC1*) of fraction I gave 20 mg α-humulene and of fraction II (TLC2) 20 mg methyl linolenoate and 10 mg 16. Fraction III gave 2 g 1 and fraction IV was separated by HPLC (HP1**)) affording eight fractions (IV/1 - IV/8). Only fraction IV/7 showed an acetoxy singlet in the ^{1}H NMR spectrum. Fraction IV/1 therefore was acetylated ($Ac_2O/CHCl_3$/DMAP, 12 h, 20°, 1 h, 70°). HP1 gave 60 mg 4Ac (R_t 2.2 min) and 20 mg 11Ac (R_t 2.0 min). After acetylation (s.a.) fraction IV/2 gave by HP3 30 mg 7Ac (R_t 1.4 min). Fraction IV/3 gave after acetylation (s.a.) by HP2 450 mg 9bAc (R_t 0.9 min), 60 mg 9aAc (R_t 2.1 min) and 20 mg 5Ac (R_t 2.6 min). After acetylation of fraction IV/4 (s.a.) HP2 gave 50 mg 9Ac (R_t 3.5 min) and 60 mg 10Ac (R_t 4.2 min.).

Fraction IV/5 gave by HP3 after acetylation (s.a.) 20 mg 8Ac (R_t 1.5 min). Fraction IV/6 contained 100 mg 1 and fraction IV/7 gave by HP4 a mixture (R_t 8.3 min) which afforded by TLC3 10 mg 12 (R_f 0.28) and 10 mg 3 (R_f 0.45). Fraction IV/8 gave after acetylation (s.a.) by HP3 15 mg 6Ac (R_t 2.9 min), 7 mg 2Ac (R_t 4.9 min) and 150 mg 3Ac (R_t 5.9 min).

The extract of the aerial parts (1 kg) of P. texana var. ambigua (collected in Mexico, voucher B.L. Turner 15377, deposited in the Herbarium of the University of Texas at Austin) gave by CC und TLC 15 mg 13, 25 mg 14 and 3 mg 15. The roots (50 g) gave 10 mg 14 and 3 mg 15. The structures were deduced by comparison of the ^{1}H NMR spectra with those of authentic material.

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*)TLC1 = petrol, TLC2 = Et_2O-petrol, 1 : 19, TLC3 = Et_2O-MeOH, 49 : 1.

**)HPLC always RP 8, flow rate 3 ml/min. HP1 = MeOH-H_2O, 7 : 3; HP2 17 : 3; HP3 9 : 1; HP4 3 : 1.

3ß,15,16-Trihydroxy-ent-pimar-7-ene (2). Isolated as its triacetate 2Ac; colourless oil; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1745, 1240 (OAc); MS m/z (rel. int.):388.261 [M - HOAc]$^+$ (21) (calc. for $C_{24}H_{36}O_4$: 388.261), 328 [388 - HOAc]$^+$ (100), 315 [388 - CH_2OAc]$^+$ (8), 268 [328 - HOAc]$^+$ (34), 185 (20), 69 (75); $[\alpha]_D^{24°}$ +7 ($CHCl_3$; c 0.56).

2α,15,16-Trihydroxy-ent-pimar-7-ene (3). Colourless gum; IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3620 (OH); MS m/z (rel. int.): 322.251 [M]$^+$ (42) (calc. for $C_{20}H_{34}O_3$: 322.251), 307 [M - Me]$^+$ (12), 304 [M - H_2O]$^+$ (82), 289 [304 - Me]$^+$ (28), 273 [304 - CH_2OH]$^+$ (72), 271 (68), 243 [304 - $CH(OH)CH_2OH$]$^+$ (100), 185 (72), 121 (86), 105 (86), 93 (88), 69 (94); $[\alpha]_D^{24°}$ +30 ($CHCl_3$; c 1.68). Acetylation (s.a.) gave 3Ac; colourless gum; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1740, 1240 (OAc); MS m/z (rel.int.): 388.261 [M - HOAc]$^+$ (100) (calc. for $C_{24}H_{36}O_4$: 388.261), 328 (84), 315 [388 - CH_2OAc]$^+$ (42), 268 (77), 185 (92), 69 (63); ^{13}C NMR ($CDCl_3$, C-1 - C-20): δ 44.8, 68.9, 35.0, 37.3, 49.8, 23.2, 122.2, 133.9, 51.5, 36.5, 19.7, 46.9, 34.6, 45.0, 71.9, 63.0, 33.4, 23.8, 23.0, 15.4; OAc: 170.9, 170.5, 170.3, 20.8, 20.9, 21.5; $[\alpha]_D^{24°}$ +29 ($CHCl_3$; c 7.18).

2α,15,16,18-Tetrahydroxy-ent-pimar-7-ene (4). Isolated as its tetraacetate 4Ac; colourless gum; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1750, 1250 (OAc); MS m/z (rel. int.): 506 [M]$^+$ (0.04), 446.267 [M - HOAc]$^+$ (12) (calc. for $C_{26}H_{38}O_6$: 446.267), 386 [446 - HOAc]$^+$ (12), 326 [386 - HOAc]$^+$ (16), 311 [326 - Me]$^+$ (14), 241 (19), 185 (100); $[\alpha]_D^{24°}$ +0.6 ($CHCl_3$; c 5.04).

3α,15,16,18-Tetrahydroxy-ent-pimar-7-ene (5). Isolated as its tetraacetate 5Ac; colourless oil; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1745, 1240 (OAc); MS m/z (rel. int.): 506 $[M]^+$ (0.3), 446.267 $[M - HOAc]^+$ (75) (calc. for $C_{26}H_{38}O_6$: 446.267), 386 $[446 - HOAc]^+$ (44), 326 $[386 - HOAc]^+$ (82), 266 $[326 - HOAc]^+$ (100), 251 $[266 - Me]^+$ (91), 185 (66), 119 (73); $[\alpha]_D^{240}$ +30 ($CHCl_3$; c 6.57).

15,16-Dihydroxy-ent-pimar-7-en-3-one (6). Isolated as its diacetate 6Ac; colourless oil; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1745, 1240 (OAc), 1710 (C=O); MS m/z (rel. int.): 344.235 $[M - HOAc]^+$ (81) (calc. for $C_{22}H_{32}O_3$: 344.235), 284 $[344 - HOAc]^+$ (100), 269 $[284 - Me]^+$ (72), 199 (72), 198 (77), 185 (73); $[\alpha]_D^{240}$ +44 ($CHCl_3$; c 1.21). To 10 mg 6Ac in 5 ml abs Et_2O, 20 mg $LiAlH_4$ was added. After 5 min dil H_2SO_4 was added, usual work-up gave 7 mg 2; colourless oil; IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3615 (OH); MS m/z (rel. int.): 322.251 $[M]^+$ (10) (calc. for $C_{20}H_{34}O_3$: 322.251), 304 (28), 273 $[304 - CH_2OH]^+$ (100), 255 (22), 243 (31), 135 (92). Acetylation (s.a.) gave 2Ac, identical with the isolated triacetate (^1H NMR).

15,16,18-Trihydroxy-ent-pimar-7-en-3-one (7). Isolated as its triacetate 7Ac; colourless gum; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1740, 1240 (OAc), 1705 (C=O); MS m/z (rel. int.): 462.262 $[M]^+$ (3) (calc. for $C_{26}H_{38}O_7$: 462.262), 402 (4), 342 (12), 282 (10), 185 (23), 169 (100); CD (MeCN): $\Delta\varepsilon_{293}$ +0.91.

15,16-Dihydroxy-ent-pimar-7-en-3-one-16-O-ß-D-glucopyranoside (8). Isolated as its pentaacetate 8Ac; colourless gum; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1750, 1230 (OAc), 1705 (C=O); MS m/z (rel. int.): 632.320 $[M]^+$ (1) (calc. for $C_{34}H_{48}O_{11}$: 632.320), 572 $[M - HOAc]^+$ (0.05), 512 $[572 - HOAc]^+$ (0.05), 452 $[512 - HOAc]^+$ (0.06), 331 [sugar part]$^+$ (21), 284 $[C_{20}H_{28}O]^+$ (20), 271 $[331 - HOAc]^+$ (6), 211 $[271 - HOAc]^+$ (4), 169 [211 - ketene]$^+$ (100); CD (MeCN): $\Delta\epsilon$ 294 +0.7.

3α,15,16-Trihydroxy-ent-pimar-7-ene-16-O-ß-D-glucopyranoside (9). Acetylation (Ac_2O/DMAP/$CHCl_3$, 2 h, 20°) gave the tetraacetate 9bAc; colourless crystals, mp 182°; IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3540 (OH), 1750 (OAc); MS m/z (rel. int.): 634.335 $[M - H_2O]^+$ (48) (calc. for $C_{34}H_{50}O_{11}$: 634.335), 616 $[634 - H_2O]^+$ (6), 574 $[634 - HOAc]^+$ (2), 331 [sugar part]$^+$ (70), 286 (71), 169 [331 - 2 x HOAc, ketene]$^+$; ^{13}C NMR (C_6D_6, C-1 - C-20): δ 31.9, 25.7, 75.8, 37.1, 44.3, 20.4, 127.1, 135.8, 51.6, 36.5, 20.3, 35.4, 35.3, 45.5, 70.3, 62.0, 28.6, 23.0, 22.8, 15.0; C-1' - C-6': δ 101.7, 68.8, 73.2, 71.8, 73.4, 73.2; OAc: 170.1, 170.0, 169.1 (2 x), 20.1, 20.2 (2 x), 20.3 (a few signals may be interchangeable); $[\alpha]_D^{24°}$ +3 ($CHCl_3$; c 1.45).

Further acetylation gave 9aAc; colourless crystals, mp 192°; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3540 (OH), 1750, 1240 (OAc); MS m/z (rel. int.): 676.346 $[M - H_2O]^+$ (37) (calc. for $C_{36}H_{52}O_{12}$: 676.346), 634 $[M - HOAc]^+$ (8), 574 $[634 - HOAc]^+$ (3), 346 [M -sugar part]$^+$ (33), 331 [sugar part]$^+$ (51), 328 $[346 - H_2O]^+$ (42), 268 $[328 - HOAc]^+$ (52), 169 [331 - 2 x HOAc, ketene]$^+$ (100).

Acetylation of 9bAc (s.a.) gave the hexaacetate 9Ac; colourless gum; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1740, 1240 (OAc); MS m/z (rel.int.): 676.346 [M - HOAc]$^+$ (14) (calc. for $C_{36}H_{52}O_{12}$: 676.346), 616 [676 - HOAc]$^+$ (2), 446 (42), 386 (40), 331 (48), 326 (55), 266 (44), 185 (62), 169 [331 - 2 x HOAc, ketene]$^+$.

2α,15,16-Trihydroxy-ent-pimar-7-ene-16-O-ß-D-glucopyranoside (10). Isolated as its hexaacetate 10Ac; colourless gum; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1745, 1240 (OAc); MS m/z (rel. int.): 676.346 [M - HOAc]$^+$ (58) (calc. for $C_{36}H_{52}O_{12}$: 676.346), 616 [676 - HOAc]$^+$ (12), 446 (5), 388 (14), 331 (66), 328 (60), 268 (55), 169 (100); $[\alpha]_D^{24°}$ -5 ($CHCl_3$; c 3.59).

3α,15,16,18-Tetrahydroxy-ent-pimar-7-ene-16-O-ß-D-glucopyranoside (11). Isolated as its heptaacetate 11Ac; colourless crystals, mp 152°; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1750, 1250 (OAc); MS m/z (rel. int.): 734.351 [M - HOAc]$^+$ (0.3) (calc. for $C_{38}H_{54}O_{14}$: 734.351), 674 [734 - HOAc]$^+$ (0.2), 614 [674 - HOAc]$^+$ (2), 446 (4), 386 (5), 331 [sugar part]$^+$ (4), 326 (3.5), 266 (6), 169 (100); $[\alpha]_D^{24°}$ +3 ($CHCl_3$; c 0.68).

14,15,16,19-Tetrahydroxy-ent-manoyloxide-19-O-acetate (12). Colourless gum; IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3540 (OH), 1745 (OAc); MS m/z (rel. int.): 380 [M - H_2O]$^+$ (0.5), 367.248 [M - CH_2OH]$^+$ (22) (calc. for $C_{21}H_{35}O_5$: 367.248), 337 [M - $CH(OH)CH_2OH$]$^+$ (64), 307 [367 - HOAc]$^+$ (21), 289 [307 - H_2O]$^+$ (19), 277 [337 - HOAc]$^+$ (29), 259 [277 - H_2O]$^+$ (62), 241 [259 - H_2O]$^+$ (20), 135 (100); ^{13}C NMR ($CDCl_3$, C-1 - C-20): δ 43.7, 18.0, 38.9, 36.9, 56.9, 20.1,

36.4, 76.1, 55.6, 36.9, 14.5, 26.1, 76.4, 74.6, 64.8, 66.9, 24.3, 27.3, 62.2, 15.8; OAc: 21.0, 171.3 (some signals may by interchangeable). Acetylation (s.a.) gave the tetraacetate 12Ac; colourless oil; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1750, 1240 (OAc); MS m/z (rel. int.): 509.275 $[M - Me]^+$ (1) (calc. for $C_{27}H_{41}O_9$: 509.275), 451 $[M - CH_2OAc]^+$ (12), 391 (26), 379 $[M - CH(OAc)CH_2OAc]^+$ (35), 331 $[391 - HOAc]^+$ (9), 313 $[331 - H_2O]^+$ (48), 301 $[319 - H_2O]^+$ (30), 241 $[301 - HOAc]^+$ (81), 135 (100).

Geranylcaprylate (16). Colourless oil; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1735 (CO_2R); MS m/z (rel.int.): 280.240 $[M]^+$ (0.1) (calc. for $C_{18}H_{32}O_2$: 280.240), 136 $[M - RCO_2H]^+$ (15), 127 $[RCO]^+$ (12), 121 $[136 - Me]^+$ (20), 93 (72), 69 (100), 68 (67); ^1H NMR ($CDCl_3$): δ 4.56 (br d, H-1), 5.36 (br t, H-2), 2.09 (m, H-4, H-5), 5.09 (br t, H-6), 1.68 (br s, H-8), 1.60 (br s, H-9), 1.77 (br s, H-10); RCO_2R: 2.29 (t, H-2'), 1.62 (tt, H-3'), 1.28 (m, H-4' - H-7'), 0.88 (t, H-8'); J [Hz]: 1,2 = 5,6 = 2',3' = 3',4' = 7',8' 7).

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Table 1. ^{1}H NMR spectral data of 3 and 2Ac - 7Ac (400 MHz, $CDCl_3$, δ-values)

H	2Ac	3	3Ac	4Ac	5Ac	6Ac	7Ac	multiplicity
1α	*	2.12	2.08	2.06	*	2.08 br d	2.00 m	ddd
1β	*	1.15	1.23	*	*	1.46 m	1.48 m	t
2α	1.63 m	3.68 tt	4.96 tt	4.48 tt	*	2.69 dt	2.68 dt	
2β					*	2.23 dt	2.31 dt	
3α	-	1.76 tt	1.77 tt	1.75 tt	4.89 br t	-	-	
3β	4.50 dd	0.98	1.06	1.05	-	-	-	m
5	1.22	1.12	1.14	1.35 m	1.61	1.53	1.50	dd
7	5.41	5.37	5.43	5.48	5.40	5.45	5.45	br dd
11	1.44 m	1.46 tt *	1.44 m	1.42 m	1.40 m	*	*	
12α	1.68	2.01	1.70	1.68	1.73	1.71	1.72	dt
12β	1.05 m	1.04	1.06 m	*	*	1.06	*	dt
14α	2.15	2.06	2.16	2.14	2.16	2.18	2.18	dd
14β	1.88	1.84	1.88	1.88	1.91	1.89	1.93	br d
15	5.17	3.68	5.17	5.14	5.18	5.21	5.20	dd
16	4.33	3.73	4.33	4.31	4.34	4.35	4.35	dd
16'	4.03	3.51	4.03	3.98	4.02	4.02	4.00	dd
17	0.87	0.88	0.92	0.90	0.93	0.94	0.93	s
18	0.92	0.96	1.00	3.78 d 3.68 d	3.99 3.80	1.12	4.17 3.88	s
19	0.93	0.93	0.97	1.02	1.10	1.11	1.09	s
20	0.96	0.81	0.93	0.99	0.97	1.05	1.07	s
OAc	2.05 (6H)	-	2.04	2.03	2.05	2.06	2.05	s
	2.01		2.01 (6H)	2.02	2.01	2.02	2.00	s
				1.99	2.00		1.99	s
				1.98	1.99			s

+) Obscured;

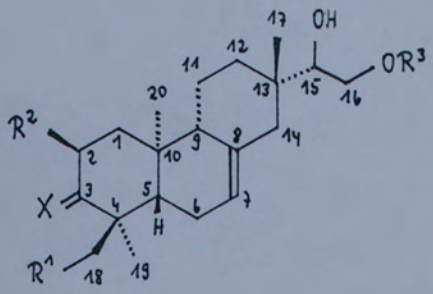
J [Hz]: Compounds 2Ac - 7Ac and 3: 5,6α = 10; 5,6β = 5; 6α,7 = 7,9 = 7,14 ~ 1.5; 6β,7 ~ 3; 11α,12α = 12α,14α ~ 3; 11β,12α = 12α,12β ~ 13; 11β,12β ~ 3; 14α,14β = 14.5; 15,16 = 9; 15,16' = 2.5; 16,16' = 11 (compounds 4Ac, 5Ac and 7Ac: 18,18' = 11; compounds 3, 3Ac and 4Ac: 1α,1β = 1β,2α = 2α,3β = 3α,3β = 12; 1α,2α = 2α,3α = 3.5; compound 2Ac: 2α,3 = 2β,3 = 3; compounds 6Ac and 7Ac: 1α,2α = 1α,2β = 3.5; 1β,2α = 2α,2β = 14.5).

Table 2. ^{1}H NMR spectral data of 8Ac, 9Ac, 9aAc, 9bAc, 10Ac, 11Ac, 12 and 12Ac (400 MHz, $CDCl_3$, δ-values)

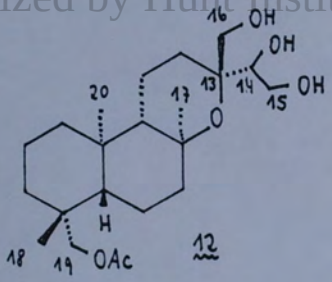
H	8Ac	9Ac	9aAc	9bAc	10Ac	11Ac	12	12Ac	npc
2α	2.69 dt	1.00 m	1.00 m	1.00 m	4.94 tt	+	+	+	
2β	2.22 dt	1.68 m	1.65 dq	1.58 dq	-	+	+	+	
3α	-	4.69 br t	4.68 br t	3.44 br t	1.77 ddd	4.89 br t	1.70 br d	1.70 br t	
3β	-	-	-	-	1.00 m	-	0.96 dt	0.95 dt	
5	1.53	1.57	+	+	1.15	+	+	+	d
7	5.39	5.38	5.33	5.31	5.39	5.33	+	+	b
14α	2.11	2.10	+	+	2.07	+	+	+	b
14β	1.86	1.89	+	+	1.85	+	3.77 dd	5.18 dd	b
15	5.10	5.09	3.85 d	3.83 d	5.05	5.08	3.73 dd 3.61 dd	4.44 dd 4.13 dd	d
16	3.84	3.84	3.67 d	3.65 d	3.81	3.84	3.42 d	4.04 d	d
16'	3.73	3.75	3.63 t	3.62 t	3.71	3.72	3.33 d	3.97 d	d
17	0.87	0.87	0.88	0.86	0.91	0.87	1.34	1.24	s
18	1.14	1.02	0.99	0.94	1.00	3.98 d 3.81 d	0.96	0.95	s
19	1.05	0.95	0.86	0.93	0.96	1.11	4.15 3.88	4.16 3.87	s
20	1.12	0.88	0.78	0.77	0.84	0.97	0.80	0.81	s
1'	4.47	4.48	4.50	4.49	4.47	4.45	-	-	d
2'	4.93	4.95	4.99	4.97	4.99	4.93	-	-	d
3'	5.19	5.20	5.20	5.18	5.16	5.18	-	-	t
4'	5.07	5.08	5.06	5.05	5.04	5.07	-	-	t
5'	3.64	3.65	3.72	3.70	3.62	3.64	-	-	d
6_1'	4.27	4.28	4.23	4.22	4.24	4.27	-	-	d
6_2'	4.14	4.15	4.14	4.13	4.11	4.13	-	-	d
OAc	2.08	2.10	2.09	2.07	2.07	2.08	2.05	2.10 (6H)	s
	2.02	2.05	2.03 (6H)	2.02	2.00	2.02		2.03	s
	2.00	2.04	2.02	2.01	1.99	2.01		2.01	s
	1.98	2.03	2.00	1.99	1.98 (6H)	2.00			s
		2.02			1.97	1.99			s
		2.00				1.98 (6H)			s

+) obscured.

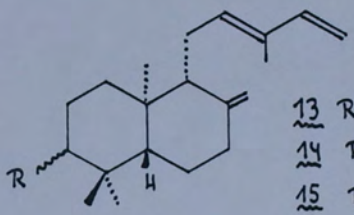
J [Hz]: Compounds 8Ac, 9Ac, 9aAc, 9bAc, 10Ac and 11Ac: 5,6α = 11; 5,6β = 4; 6α,7 = 7,9 = 7,14 ~ 1.5; 6β,7 ~ 3; 14α,14β = 14; 15,16 = 9; 15,16' = 2.5; 16,16' = 11; 1',2' = 8; 2',3' = 3',4' = 4',5' = 9.5; 5',6_1' = 4; 5',6_2' = 2.5; 6_1',6_2' = 12.5; (compounds 8Ac: 1α,2α = 5; 1α,2β = 3; 1β,2α = 2α,2β = 15; compounds 9Ac, 9aAc, 9bAc and 11Ac: 2α,3 = 2β,3 ~ 2.5; compounds 9aAc and 9bAc: 1α,2β = 1β,2β = 2.5; 2α,2β = 14; 15,16 = 9; 15,16' = 10; compound 10Ac: 1α,2α = 2α,3α = 3.5; 1β,2α = 2α,3β = 12; compounds 7Ac and 11Ac: 18,18' = 11; compounds 12 and 12Ac: 2α,3α = 4; 2α,3β = 3α,3β = 13; 14,15 = 3.5; 14,15' = 5; 15,15' = 16,16' = 19,19' = 11.



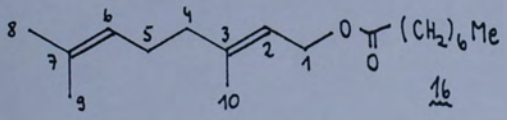
	1	2	3	4	5	6	7	8	9	10	11
R^1	H	H	H	OH	OH	H	OH	H	H	H	OH
R^2	H	H	OH	OH	H	H	H	H	H	OH	H
R^3	H	H	H	H	H	H	H	G*	G*	G*	G*
X	βOH,H	αOH,H	H_2	H_2	βOH,H	=O	=O	=O	βOH,H	H_2	βOH,H



12

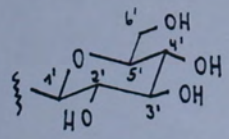


13 R = αOAc
14 R = αOH
15 R = βOH



16

G =



1Ac - 12Ac are the peracetylated derivatives, 9aAc is the 3,2',3',4',6' pentaacetate, 9bAc the 2',3',4',6' tetraacetate

FURTHER PYRONES AND OTHER CONSTITUENTS FROM PODOLEPIS SPECIES

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Key Word Index - Podolepis canescens, P. capillaris, P. lessonii, P. longipedata, P. rugata; Compositae; pyrones, lignans, coumarins, sesquiterpenes, bisabolol derivatives.

Abstract - The investigation of five Australian Podolepis species afforded in addtion to two previously described pyrones seven new ones. Furthermore two new lignans, one unusual oxidation product of hydroxy obliquin as well as three sesquiterpenes derived from bisabolol were isolated. The structures were determined by spectroscopic methods.

INTRODUCTION

From the Australian genus Podolepis so far only one species has been investigated chemically, affording tetrasubstituted γ-pyrones [1]. We now present results on five further species.

RESULTS AND DISCUSSION

The aerial parts of Podolepis canescens Cunn. ex DC and of P. lessonii (Cass.) Benth. gave, both, the known lignans 3a [2], 3b [3], 3d [4] and 3e [5] while those of P. longipedata A. Cunn. ex DC afforded, in addition to the pyrones 1a [1] and 1b [1], large amount of 1i. Furthermore 3a, 3b and 3c [6] were isolated. The roots of P. rugata Labill. var. rugata gave, in addition to podopyrone (1a), six new pyrones 1c - 1h, sesamin (2a) [7] and two closely related derivatives 2b and 2c, further lignans 3d, 3e and 3f [8], the obliquins 4a [9] and 4b [5] and 4c, an oxidation product of the former, as well as the sesquiterpenes 5a - 5c. The aerial parts gave the same compounds except 1c and instead of 3d - 3f the lignans 3a and 3b. From P. capillaris no characteristic compound could be obtained.

The ^{1}H NMR spectra of 1c and 1f respectively (Table 1) differed from that of podopyrone (1a) only in the signals for an ethyl group which replaced one of the methyl singlets. The relative position of the substituents followed from the nOe effect between H-7 and H-1' and the length of the side chain from the mass spectra. The ^{13}C NMR data (Table 2) are also in accordance with the structure.

The ^{1}H NMR spectra of 1c/d and 1g/h (Table 1) differed also in the signals for a methyl and ethyl group, respectively. From the ^{13}C NMR spectra (Table 2) of 1g/h the presence of an unsaturated keto group (δ 195.9 s) could be deduced which only could be placed at C-1'. This explained also the down field shift of H-7 methyl singlet in the proton spectra compared with podopyrone. In the case of 1h the arrangement of the substituents was ensured by means of selective INEPT experiments through the long range coupling. In this way the protons of the methoxy group were connected with C-2, H-7 with C-4, C-5 and C-6 and H-8 with C-2, C-3 and C-4. Again, the length of the side chain followed from the mass spectrum. The ^{1}H NMR spectrum of 1i (Table 1) was again very similar to that of podopyrone. An additional low field singlet at δ 2.12 s and the absence of the terminal methyl triplet of the side chain required a methyl ketone which was further supported by the ^{13}C NMR spectrum (Table 2). A similar compound with an ethyl group at C-3 was isolated from P. hieracioides [1].

The structure of the sesamin derivatives 2b and 2c followed from the ^{1}H NMR spectra (s. Experimental). The additional methoxy group in 2b led to non-equivalence of all protons which could be assigned by spin deocupling. The relative position of the methoxy group and the stereochemistry were established by nOe experiments. Thus the irradiation of methoxy signals gave an effect with H-7 and not with H-6. Further effects were observed between H-8 and H-9_1, between H-7, H-5 and H-9_2, between H-8' and H-9_1' as well as between H-7', H-3', H-5' and H-9_2'. The symmetrical arrangement of the substituents in 2c led to an identical coupling pattern as in the spectrum of sesamin. The relative position of the methoxy group was not further established but was very likely on biogenetical consideration.

Except for

Apart from the differences in chemical shifts, was the ^{1}H NMR spectrum of 4a (s. Experimental) identical with that of methoxy obliquine. As the mass spectrum required one more oxygen, the proposed structure was likely. An isomer with a methoxy group at C-4a could be excluded due to the missing nOe with H-4 on irradiation of the methoxy signal. The ^{13}C NMR spectrum (s. Experi- mental) supported the structure. We have named compound 4c podorugatin.

The ^{1}H NMR spectra of 5a and 5b (s. Experimental) were very similar to those of the known aldehydes [10,11]. The absence of the aldehyde signals and additional methyl singlets at δ 3.73 and 3.83 respectively, indicated carbomethoxy groups.

The up field shift of the olefinic proton signal in the spectrum of 5b and the broad singlet at δ 4.70 (2H) required an acyloxy methylene group. The nature of the ester group followed from the typical signals (s. Experimental).

The chemistry of five investigated Podolepis species is not uniform. Obviously the pyrones are characteristic as well as the lignans. Obliquins and pyrone derivatives are common in Helichrysum but the relevance of bisabolene derivatives is not yet clear. The placement of Podolepis next to the Australian Helichrysum species [12] is supported by the chemistry. Further studies may show whether the Australian Athrixia species are chemically related as they are proposed to be close to Podolepis [12].

[13] is reflected in their chemistry.

The close relationship suggested between Podolepis and

EXPERIMENTAL

The air dried plant material (voucher are deposited in the US National Herbarium, Washington) was extracted with MeOH-Et_2O-petrol, 1 : 1 : 1, and the extracts obtained were separated by CC and further by TLC and HPLC (always RP 8, ca. 100 bar, MeOH-H_2O mixtures in different ratios: HP1: 9 : 1; HP2: 17 : 3; HP3: 4 : 1; HP4: 7 : 3; HP5: 13 :7). The conditions of the final purification of new compounds are given in the parenthesis (s. below).

The extract of Podolepis canescens (200 g, voucher RMK 9563) gave 30 mg 3a, 440 mg 3b, 330 mg 3d and 60 mg 3e. P. lessonii (100 g, voucher RMK 9539) gave 72 mg 3a, 140 mg 3b, 450 mg 3d and 110 mg 3e. P. longipedata (480 g, voucher 86/0192) afforded 300 mg 1a, 50 mg 1b, 800 mg 1i (HP4, R_t 19 min), 10 mg 3a, 33 mg 3b and 50 mg 3c. From P. rugata (voucher RMK 9602), both, aerial parts and the roots were investigated. The amounts from the roots are given in parenthesis. 900 g aerial parts (65 g roots) gave 60 mg (15 mg) 1a, 2 mg (13 mg) 1d (HP2, R_t 12.2 min), 7 mg (2 mg) 1e (HP1, R_t 13.4 min), 15 mg (3 mg) 1f (HP1, R_t 15.6 min), 12 mg (5 mg) 1g (HP3, R_t 18.6 min), 22 mg (19 mg) 1h (HP3, R_t 25 min), 9 mg (15 mg) 2a, 13 mg (12 mg) 2b (HP3, R_t 8.2 min), 10 mg (8 mg) 2c (HP3, R_t 9.8 min), 300 mg 3a, 7 mg 3b, 150 mg (7 mg) 4a, 23 mg (4 mg) 4b, 4 mg (4 mg) 4c (HP5, R_t 8.1), 2 mg (2 mg) 5a (TLC, CH_2Cl-Et_2O, 97 : 3, R_f 0.4), 2 mg (21 mg) 5c (TLC as 5a, R_f 0.6) and 2 mg (12 mg) 5b (HP5, R_t 16.3 min). Additionally the roots gave 4 mg 1c (HP2, R_t 10.2 min), 3 mg 3d, 3 mg 3e as well as 3 mg 3f. Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material.

SESQUITERPENE LACTONES AND OTHER CONSTITUENTS FROM URSINIA SPECIES

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Key Word Index - Ursinia sp.; Compositae; sesquiterpene lactones; germacranolides; guaianolides; rearranged eudesmanolide, guaiane, eudesmane and eremophilane derivatives; fulvenes, farnesol derivatives; furosesquiterpene.

Abstract - From 12 Ursinia species in addition to known compounds 31 new sesquiterpene lactones, 10 being germacranolides, 19 guaianolides, one eudesmanolide and a rearranged one, were isolated. Furthermore, seven sesquiterpene acids and methyl

esters, including two fulvenes and a rearranged eudesmane, a nerolidol and seven farnesol derivatives, a furosesquiterpene derived from dehydrolasiospermane, three eudesmane and three eremophilane derivatives as well as a triynene were present. The structures were elucidated by high field NMR techniques. The chemistry supports the placement of the genus in the tribe Anthemideae best as a subtribe together with related South African genera.

INTRODUCTION

The nearly 40 Ursinia species form a very natural genus growing throughout South Africa and extending with a few species into East Africa. Its placement in a tribe is still not completely solved. Traditionally, it was a part of the tribe Arctoteae [1] but later it was placed in the Anthemideae [2] as the genus resembles the latter in habit and several other morphological features though the ligul epidermis type differed from that of the Anthemideae [3]. The pollen type is more close to the Arctoteae [4] but different [4,5] and therefore has been excluded from the latter tribe [6]. The problem of placement already has been discussed in a revision of Ursinia [7] and more detailed in a tribal revision [8] leading to the placement of the genus in the monogeneric tribe Ursinieae. Of the various genera lacking the pollen type of the Anthemideae, Ursinia in the only one showing any real relationship, having habit, coralla lobes and coralla glands of the same type. Stylebranches are like those of

the Anthemideae. Therefore remains the choice of treatment the genus as a member of the Anthemideae differing by two very basic characters, or treating it as a separate but related tribe [8].

So far already 12 Ursinia species have been studied chemically [9 - 16], ten of them gave very characteristic furosesquiterpenes, also present in the related South African genera Athanasia [17], Phymaspermum [17], Eumorphia [18], Asaemia [19], Gymnopentzia [19], Stilpnophytum [17], Hymenolepis [20] and Lasiospermum [21]. However, six Ursinia species also contain sesquiterpene lactones, among others the ursiniolides with cis-anellation of the lactone ring [11 - 14]. To get a more clear picture we therefore have studied the constituents of 12 Ursinia species, four of them being studied previously. The results are presented in this paper.

RESULTS AND DISCUSSION

The roots of U. abrotanifolia Spreng. gave the furosesquiterpenes 88 [21], 91 [9] and 92 [22], coumarin, 106 and the triterpene 108 [23] while the aerial parts afforded also 91, some widespread hydrocarbons (s. Experimental), spathulenol, the sesquiterpene lactones laurenobiolide and the related lactones 29 [24], 31 [25], 32]25], 33 [26], 34 [26] and 35 [27], the guaianolide 46 [28] and the eudesmanolide 70. The structure of 70 followed from its ^{1}H NMR spectrum (s. Experimental) which was in part similar to that of dentatin A [29]. However, the exo-methylene proton signals were replaced by a methyl singlet at δ1.39. The ß-orientation of the 4-methyl group followed from the NOE with H-6.

A reinvestigation of the aerial parts of U. anthemoides (L.) Poiret, which has been studied several times [11 - 14], collected in Australia, afforded the known ursiniolides 19 [14] and 20 [14] as well as the 3α-acetoxy derivative 21, the farnesol derivatives 93 - 99 and the triynene 103.

The structure of 21 follows from its ^{1}H NMR spectrum (Table 1) which was very similar to those of other ursiniolides. The observed coupling of H-3 indicated an α-acetoxy group. The ^{1}H NMR spectra of 93 (Table 2) showed that we were dealing with a disubstituted farnesol derivative with one acetoxy group. Spin decoupling indicated that the latter most likely was at C-8. This and the configuration of the double bonds was established by NOED, especially, by clear effects between H-1 and H-15, H-10 and H-12 as well as between H-13 and H-9. As H-9 was coupled with the proton under the acetoxy group the structure was settled. Similarly, the structures of 94 - 99 followed from their ^{1}H NMR spectra (Table 2). Configurations of the double bond again were determined by NOED and the position of the acetoxy groups followed from the down field shifts of the relevante signals.

The UV spectrum of 103 already showed that a triynene was present, while the ^{1}H NMR data required a senecioate of deca-4,6,8-triyn-2E-ene-1-ol (s. Experimental).

The aerial parts of U. cakilefolia DC gave the furosesquiterpenes 88 and 92 [9], umbelliferon methyl ether, the sesquiterpene lactone costunolide (1) [22], the ursiniolides 14 [13], 15 [13], 16 [13], 17 [14], 18, 22 [30], the guaianolides 38, 40 and 41 and the eudesmanolide 63 [31].

The structure of 18 easily could be deduced from its ^{1}H NMR spectrum (Table 1) which was very close to that of 15, only the H-3 signal being up field shifted and the acetate singlet being absent.

The ^{1}H NMR spectrum of 38 (Table 3) indicated an 8α-angeloyloxy derivative related to zuurbergenin where the angelate group is replaced by an acetoxy group [32]. The ^{1}H NMR spectrum of 41 (Table 3) was in part similar to that of 38. However, the situation in the five membered ring was changed. The olefinic methyl signal was replaced by singlet at δ 1.46 and a pair of doublets at δ 6.33 and 5.95 required a 2,3-double bond. Accordingly, lactone 38 was transformed by allylic oxidation to a 4-hydroxy derivative. The configuration at C-4 could be deduced from comparison of the chemical shifts with those of the corresponding 11α,13-dihydro derivative where the stereochemistry was determined by X-ray analysis [16]. As the ^{1}H NMR data of 40 (Table 3) only differed in some small chemical shift differences from that of 41 the presence of a 4-epi-isomer was very likely. Accordingly, H-6 was slightly more down field in the case of 41 due to the deshielding effect of the ß-hydroxy group. Similarly, the α-methyl group was deshielded by the lactone oxygen if compared with the shifts of lactone 40.

The roots of U. dentata (L.) Poir. gave coumarin, the guaianolides 49 - 52 and 100 while the aerial parts afforded in addition to the triterpenes taraxasteryl and lupeyl acetate also the guaianolides 49 - 52 and 8-acetoxynerolidol (100). The structures of 49 - 51 followed from their ^{1}H NMR spectra (Table 3) though a complete separation of the mixture was not achieved.

Spin decoupling led to the proposed sequences. The stereochemistry followed from the comparison of the data with those of tanaparthin α-peroxide [33] and from the observed chemical shifts of H-2, H-3 and H-6, which clearly differed from those of ß-peroxide [33]. The ^{1}H NMR of 51 is identical with an angelate isolated from an Athanasia species [34], where, however, the configuration at C-1 and C-4 had to be changed [35]. The corresponding precursors, a 1,3,9-triene, was not observed. Therefore the lactones most likely are no artifacts. The structure of 100 followed from its ^{1}H NMR spectrum (s. Experimental) and its ^{13}C NMR data (Table 4) where all signals could be assigned by 2D hetero COSY and COLOC. Spin decoupling and NOED established the configuration of the Δ^6double bond and the position of the acetoxy group (effect between H-6 and H-8, not with H-14).

The aerial parts of U. eckloniana (Sond.) N.E.Br. gave cycloartenyl acetate, ß-amyrin, ß-farnesene, the isovalerates 101 and 102 [36], the ß-thujene derivative 105 [37], the seco caryophyllene derivative 104 [38], the eudesmanolides 64 [39], 65 [38], 66 [38], 67 [38], 68 [40] and 69 [41], the methyl esters 74 [42], 76 [43], 77, 79 and 80 as well as the rearranged lactone 71.

The ^{1}H NMR spectrum of 77 (Table 6) is nearly identical with that of 76. In agreement with a low field singlet and a fragment at m/z 247 [M - OOH] the presence of the corresponding hydroperoxide was very likely.

The structure of 79 followed from its ^{1}H NMR spectrum (Table 6) which shows similarities to that of a seco eudesmanolide (65a)

derived from isoalantolactone [44]. This also was supported by the base peak (m/z 196) in the ms of 79 which is formed by a McLafferty rearrangement by loss of acetone.

The methyl ester 80 most likely is formed by aldol condensation of 79. The ^{1}H NMR data (Table 6) nicely agree with the proposed structure.

The structure of the unusual lactone 71 could be deduced from its ^{1}H NMR spectrum (Table 5) and careful spin decoupling leading to sequences which only could be combined to the structure 71, a new type of sesquiterpene lactone, which most likely is formed starting with 65a via aldol condensation and elimination of water (s. Scheme). Lactone 71 we have named 9-oxo-jasoniolide as 11-hydroxyjasionone, a 11-hydroxy-5-ketone, has been isolated from a Jasonia species [45].

The aerial parts of U. nana DC gave in addition to widespread compounds (s. Experimental) umbelliferone methyl ether, methyl dihydrocaffeoate, the furosesquiterpene 88 and the sesquiterpene lactones 13 [46], 54 - 57, 59 [16], 61 and 62.

The structure of 54 was deduced from its ^{1}H NMR spectrum (Table 3). A doublet at δ 4.01 was due to H-6 as shown by spin decoupling. An olefinic proton (δ 5.80) was coupled with a proton under an oxygen function (δ 4.70). The down field shift of the latter required a position between two double bonds. The presence of a 2-methoxy group was established by a NOE between H-2 and the methoxy group. NOE's between H-2 and H-6 as well as between H-7 and H-11 required the proposed stereochemistry. The ^{1}H NMR spectrum of 55 (Table 3) differed from that of 54 by the missing H-2 and methoxy signals and the the down field shfit of H-3, H-14 and H-15, typical for cross conjugated 2-keto derivatives.

The ^1H NMR spectrum of 56 (Table 3) indicated the presence of a guaia-3,10(14)-diene-12,6α-olide with two hydroxy groups (δ 3.02 and 3.06) which only could be placed at C-1 and C-5. The absence of NOE's between H-6 and the hydroxyl required the α-orientation. A NOE of H-7 with H-11 finally established the complete stereochemistry.

The molecular formula of lactone 57 was $C_{16}H_{22}O_5$ and the ^1H NMR spectrum (Table 3) indicated the presence of a methoxy guaianolide with no double bonds. Accordingly, the molecular formula required five rings. The ^{13}C NMR spectrum (Table 4) supports the presence of two epoxides. All data agree with the presence of guaianolide 57 or 58. Considerations of models and the observed NOE's ruled out the latter possibility. Especially, the NOE of H-15 with H-6 and H-3 is only possible with structure 57. The NOE's of the methoxy group with H-9β, of H-6 with H-8β and of H-7 with H-11 established the configuration of the remaining chiral centers. The ^{13}C NMR spectrum (Table 4) supports the structure.

Lactone 61 also is a 11α,13-dihydro-cis-guaianolide as followed from the ^1H NMR data (Table 5). The downfield shift of H-14 and H-15 indicated oxygen functions at C-4 and C-5 while the missing coupling $J_{5,6}$ required such a function at C-5. An olefinic proton (δ 5.76) showed a vicinal coupling with double doublet at δ 4.38 which collapsed to a doublet on irradiaiton of a doublet at δ 1.66 or deuterium exchange. Accordingly, a hydrogen bonded hydroxy group was very likely. NOE's of H-15 with H-6, of methoxy with H-6, H-2 and H-15, of H-7 with H-11 and of H-3 with H-15 established the proposed structure and stereochemistry.

The ^1H NMR spectrum of 62 (Table 5) was in part similar to that of 61. However, the situation of the cyclopentane ring was different. The olefinic proton was replaced by a broadened singlet at δ 4.05 which showed a small coupling with a broadened singlet at δ 3.78. Furthermore, two methoxy singlets were visible. The structure and the stereochemistry could be established by the observed NOE's (H-14 with 10-OMe and H-2, H-2 with 2-OMe and H-14, H-7 with both methoxy groups, H-13 with H-8β). The ^{13}C NMR (Table 4) also supports the structure of this highly oxygenated guaianolide. In a previous investigation [15] also several sesquiterpene lactones were isolated. However, they differed in substitutions.

The aerial parts of U. nudicaulis (Thunb.) N.E.Br. collected at the Viljoen's Pass, R.S.A., gave germacrene D, taraxasteryl acetate, the ketone 104, the sesquiterpene lactones 5 [47], 37 [48], 39 [49], 42 - 45, 47, 48, 53, 60 [48] and the acids 72 and 73.

In the ^1H NMR spectrum of the crude polar fraction compounds 72 and 73 were the main constituents. However, during separation by TLC on SiO_2 only 60 [48] could be identified. After esterification of the crude mixture the methyl esters (72a and 73a) were isolated. The ^1H NMR spectra of these esters (Table 6) which could not be separated, were very similar. As a 2 : 1 mixture was present all signals could be assigned. The absence of the exomethylene proton signals in the spectrum of 73a indicated the difference of the esters. The signals of the olefinic protons and spin decoupling showed that conjugated tetraenes with a fulvene arrangement were present. The ^{13}C NMR spectra of 72a and 73a (Table 4) also support the structure. Most likely the acid 72 is transformed to the lactones 60 by autocatalytic proton attack as shown in the Scheme.

The ^{1}H NMR spectrum of 43 (Table 2) clearly shows that we were dealing with an isomer of 60, the Δ^4bond being replaced by a 4(15)- double bond. Accordingly, one olefinic methyl signal was replaced by a pair of broadened singlets at δ 5.26 and 5.15 and the H-6 signal now is a triplet with trans-diaxial couplings indicating the presence of a trans-lactone.

The ^{1}H NMR spectrum of 44 (Table 2) is in part close to that of 43. The presence of a 11α,13-dihydroguaianolide follows from the doublet at δ 1.19 which showed a NOE with H-6 requiring a 11ß-methyl. Furthermore, the signals of the exomethylene protons (H-15) were replaced by a methyl singlet at δ 1.58 and that of H-14 by a pair of broadened doublets at δ 4.69 and 4.63. As H-15 showed NOE's with H-5 and H-3 the configuration at C-4 was settled. The ^{1}H NMR data (Table 2) of 42 were in part similar to those of 43 and 44. A singlet at δ 8.01 indicated a hydroperoxide and a singlet at δ 3.34 a methoxy group spin decoupling showed that the latter was at C-9. This was supported by a NOE between H-9, H-8 and methoxy methyl. A NOE between H-15, H-5 and H-3 established the configuration at C-4.

Lactone 45 obviously is formed by an ene-reaction of 37 with oxygen. The ^{1}H NMR data (Table 2) showed a pair of double doublet of quartets (H-2) both coupling with an olefinic proton and methyl, while a low field singlet at δ 7.47 required a hydroperoxide. Spin decoupling further showed that a Δ^9double bond was present. A NOE between OOH and H-5 established the configuration at C-1 and C-5 as H-5 showed a trans-diaxial coupling with H-6.

The ^{1}H NMR spectra of 47 and 48 (Table 3) showed that these lactones only differ in the presence and absence of a 11(13)-double bond. A pair of doublets at δ 6.22 and 6.31 and the

molecular formula ($C_{15}H_{16}O_4$) required an endoperoxide bridge between C-1 and C-4. The chemical shifts and their differences of H-2 and H-3 required an α-peroxide as in the epimeric ß-peroxides the olefinic proton signals appear at δ 6.67 and 6.41 [33]. Furthermore, a ß-ethylene bridge shields H-6 by about 0.6 ppm.

The ^1H NMR spectrum of 53 (Table 3) required the presence of a 11,13-dihydroguaianolide with two methyls on oxygen bearing carbons, a methoxy group and a 2,3-double bond. As H-5 showed only one vicinal coupling one oxygen function was at C-1. NOE's of H-13 with H-6 indicates the configuration at C-11. An effect of methoxy with H-5 and H-2 required a 1α-methoxy group. Further effects between H-14 and H-9 as well as between H-15 and H-5 established the proposed stereochemistry. The ^{13}C NMR data (Table 4) also support the structure.

A sample of U. nudicaulis collected near Humansdorp gave different lactones. In addition to germacrene D, caryophyllene and taraxasteryl acetate the germacranolides 1, 2 [50], 3 [51], 4 [26], laurenobiolide [52] and 27 were isolated. The ^1H NMR spectrum of 27 (Table 1) was similar to that of 28. The presence of the 11,13-dihydro derivative of the latter followed from the corrresponding signals. The NOE of H-13 with H-6 and H-8 establish the configuration at C-11.

From the aerial parts of U. rigidula (DC) N.E.Br. taraxasteryl and lupeyl acetate, sitosterin and the germacranolides laurenobiolide, 28 [25] in very high concentration, and 26 were isolated. The structure of 26 easily could be deduced from its ^1H NMR spectrum (Table 1) which, of course, differed from that of 28 mainly by the down field shift of H-6 and the presence of the typical tiglate signals.

The aerial parts of U. sericea N.E.Br. gave caryophyllene, dehydrolasiospermane (88) [21], the isovaleryloxy derivative 89, the eudesmanes isointermedeol 53 and 10-epi-γ-eudesmol [55] and the germacranolides laurenobiolide, 2, 7 [54], 8, 12 [49], 23 [56], 24 [57], 25, 27 and 30 [58].

The ^{1}H NMR spectrum of 89 (s. Experimental) was very similar to that of 88. A new low field doublet of triplet at δ 5.63, a pair of double doublets around δ 2.70 and typical isovalerate signals indicated the presence of a 5-isovaleryloxy derivative of 88.

The ^{1}H NMR spectrum of 8 (Table 1) was in part similar to that of 2. The presence of a 4,5-epoxide and a 11,3-dihydro derivative followed from the replacement of the signals of olefinic protons by a doublet at δ 2.66 (H-5), a methyl doublet at δ 1.44 (H-13) and a double quartet at δ 2.90 (H-11). The stereochemistry was established by the observed NOE's (H-14 with H-15, H-2β and H-8, H-15 with H-14 and H-6, H-5 with H-1 and H-7, H-11 with H-6 and H-8).

Compound 25 is a dihydro derivative of laurenobiolide. While the ^{1}H NMR of the latter is highly broadened at room temperature that of 25 (Table 1) showed a few broadened signals. Therefore spin decoupling allowed the assignment of all signals. The configuration at C-11 followed from the NOE of H-13 with H-6 and H-8 while effects of H-1 with H-5 and H-9α, of H-14 with H-6 and H-8, of H-15 with H-2β and H-6 as well as of H-7 with H-11, H-1 and H-5 indicated an U.U-conformation.

The aerial parts of U. speciosa DC gave several widespread compounds (s. Experimental), the furosesquiterpene 91 [9], the triynene 103 and large amounts of 15 [13] and 21.

The aerial parts of U. tenuifolia DC var. tenuifolia gave the ketone 90 [21], the germacranolides 6 and 9 - 11 and the methyl esters 75 and 78.

The ^{1}H NMR spectrum of 6 (Table 1) was highly broadened at room temperature but at elevated temperature in a mixture of $CDCl_3/C_6D_6$ all signals could be assigned by spin decoupling which led to sequences which only agree with structure 6. The stereochemistry was deduced from the observed couplings and by NOED (H-5 with H-3 and H-7, H-8 with H-14, H-6 with H-8 and H-15).

The ^{1}H NMR spectra of 9 and 10 (Table 1) were similar. In that of 10 a singlet at δ 7.90 indicated the presence of a hydroperoxide. In both cases only at elevated temperature all signals could be assigned by spin decoupling leading to sequences which indicated that we were dealing with oxidation products of 6. An ene-reaction with oxygen leads to 10 and reduction would give the lactone 9. The stereochemistry again was estabished by NOED (H-1 with H-3, H-14 with H-8, H-5 with H-3 and H-7). These data show that for these lactones also the U.U- conformation is preferred. The ^{1}H NMR spectrum of 11 (Table 1) differed from that of 9 by the absence of the H-1 signal and the down field shift of H-14 and H-2. All data therefore agree with the presence of the corresponding 1-keto derivative 11. Also for this ketone the U.U-conformation is the preferred one as followed from the observed NOE's (H-14 with H-8 and H-5 with H-3).

The ^{1}H NMR spectrum of 78 (Table 6) indicated the presence of a hydroxy derivative of the methyl ester of isocostic acid. Accordingly, most signals were close to those of the latter. An additional broadened doublet at δ 4.85 in the spectrum of 78

required a 6-hydroxy group as the latter showed a small coupling with H-7 (2 Hz) which also indicated the ß-orientation of the hydroxy group. In the ^{1}H NMR spectrum of 75 (Table 6) a singlet at δ 7.97 and the replacement of the olefinic methyl signal by those of exomethylene protons indicated that this lactone was the corresponding hydroperoxide formed by an ene-reaction of 78 with oxygen. The observed down field shift of H-3α in the spectrum of 75, if compared with that of 78, required a 5α-hydroperoxide.

The aerial parts of U. trifida Less. gave coumarin, ß-farnesene, the triketone 107 [59], the triterpene 108 [23], the eudesmane derivatives 81 - 83 and the eremophilane derivatives 84 - 87.

The structure of 81 followed from its ^{1}H NMR spectrum (Table 8) and NOED by clear effects between H-14, H-15 (4%), H-2α (5%), H-8α (5%), H-6α (7%) and H-1α (3%), between H-15, H-14 (4%), H-3α (4%), H-6α (8%) and H-2α (5%), between 5-OH, H-11 (4%), H-3ß (3%), H-6ß (3%) and H-12 (2%) as well as between 4-OH, H-3ß (2%) and H-6ß (2%). Both signals of the hydroxy protons are unusual sharp which may indicate double hydrogen bonds between the hydroxy protons. The axial orientation of the isopropyl group followed from the observed couplings for H-6 and H-8 with H-7. The ^{13}C NMR data also support the structure (Table 9).

Similar the structure of 82 could be deduced from the ^{1}H NMR (Table 8) and ^{13}C NMR data (Table 9). However, in this case the couplings of H-7 with H-8ax only was visible after addition of Eu(fod)$_3$ which again requied an axial orientation of the side chain.

The ^{1}H and ^{13}C NMR data of 83 (Tables 8 and 9) clearly indicated the presence of a hydrocarbon with two conjugated double bonds. As two low field broadened doublets (δ 5.51 and

5.56) were visible a 3,5-diene was most likely. As irradiation at 5.56 changed the multiplet at 1.95, which itself was coupled with H-11 (1.61 dqq), this assumption was established. The coupling $J_{6,7}$ supports the proposed configuration at C-7 which also is very likely as the compounds 81 - 83 surely are closely related. Furthermore, the chemical shift of C-9 agrees with the presence of an axial isopropyl group.

The ^1H NMR spectrum of 84 (Table 8) required an eremophilane derivatives as the methyl singlets at δ 0.95 and 1.02 together with the presence of an allylic alcohol can not be combined with an eudesmane derivative. Spin decoupling allowed the assignment of all signals. The resulting sequences required the proposed structure while the stereochemistry was deduced from the observed NOE's [H-7 with H-14 (3%), H-15 with H-3 (5%), H-3β (4%), H-6 (4%) and H-6β (3%)].

The spectral data of 85 (Tables 8 and 9) showed that we were dealing with the correspoding 2-keto derivative of 84 which with the same position optical rotation already has been isolated from a Geigeria species [60], where the absolute configuration was not determined. A negative Cotton-effect supports the proposed absolute configuration of 85 as the helicity rule should be applicable.

A negative Cotton-effect also was observed in the case of 87. The NMR data (Tables 8 and 9) showed that again a 2-keto eremophilane derivative was present. Spin decoupling indicated that a hydroxy group was at C-8. A second one has to be placed at C-11 as H-12 and H-13 now were singlets and the H-11 signal was absent. The stereochemistry followed from the observed coupling of H-4 and H-8.

The ^{1}H NMR data of 86 (Table 8) indicated that a triol derived from 87 was present. The coupling of H-2 required an axial orientation. The observed NOE's [H-4 with H-2 (5%), H-6ß with H-4 (7%) and H-8 (4%), H-14 with H-7 (7%) and H-3α (6%)] established the stereochemistry at all chiral centers. The ketone 86 is closely related to the 8-desoxy derivative with identical stereochemistry isolated from a Teucrium species [61]. The ^{1}H NMR data are of course in part similar.

The roots of U. trifida contain dehydrolasiospermane (88), ß-farnesene, large amounts of the diol 82 and the triterpene 108.

The overall picture of the chemistry of the genus Ursinia shows that furosesquiterpenes and highly oxygenated sesquiterpene lactones are characteristic for this genus. However, a large variety of lactones are present. Most widespread are germacranolides and guaianolides while eudesmanolides are rare. The characteristic ursiniolides, with a 12,6ß-lactone moiety, so far only have been isolated from four species. Remarkable is the high concentration of these lactones in U. speciosa (3% of air dried aerial parts) while the lactone concentration in the other species usually is low. Exceptions are the germacranolide 28 in U. rigidula and laurenobiolide in U. sericae. Only from U. trifida no lactones were isolated, they are replaced by eudesmane and eremophilane derivatives, but the roots contain the typical furosesquiterpene 88. As in several genera of the Anthemideae 11,13-dihydrosesquiterpene lactones are relatively common. All chemical data suggest the placement of Ursinia together with the related woody South African genera (s. introduction) in a new subtribe of Anthemideae.

EXPERIMENTAL

The air dried plant material was extracted with MeOH-Et_2O-petrol, 1 : 1 : 1 and the defatted extracts (MeOH, -20°) were separated as reported previously [62]. Conditions of final purification are given with the data of the new compounds. Isolated constituents are summarized in Table 10. Known compunds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material or with lit. data.

3ß-Hydroxy-8α-isobutyryloxycostunolide (6). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3500 (OH), 1780 (γ-lacone), 1735 (CO_2R); MS m/z (rel. int.): 246 [M - RCO_2H]$^+$ (1), 204 (12), 165 (18), 85 (62), 71 [RCO]$^+$ (24), 57 (100); HPLC: MeOH-H_2O, 7 : 3, R_t 10.3 min.

8α-Hydroxy-4α,5ß-epoxy-11ßH-germacr-1(10)E-en-12,6α-olide (8). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3400 (OH), 1795 (γ-lactone); MS m/z (rel. int.): 266.152 [M]$^+$ (4.5) (calc. for $C_{15}H_{22}O_4$: 266.152), 248 [M - H_2O]$^+$ (22), 233 [248 - Me]$^+$ (12), 91 (100), 55 (98); TLC: Et_2O-petrol, 3 : 1, R_f 0.15.

1ß,3ß-Dihydroxy-8α-isobutyryloxygermacra-4E,10(14),11(13)-trien-12,6α-olide (9). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3420 (OH), 1780 (γ-lactone), 1730 (CO_2R); MS m/z (rel. int.): 350 [M]$^+$ (0.2), 262.121 [M - RCO_2H]$^+$ (2) (calc. for $C_{15}H_{18}O_4$: 262.121), 244 [262 - H_2O]$^+$ (4), 173 (12), 91 (28), 71 [RCO]$^+$ (100); HPLC: MeOH-H_2O, 3 : 2, R_t 7.8 min.

1ß-Hydroperoxy-3ß-hydroxy-8α-isobutyryloxygermacra-4E,10(14),11(13)-trien-12,6α-olide (10). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3380 (OH), 1770 (γ-lactone), 1730 (CO_2R); MS m/z (rel. int.): 278 [M - RCO_2H]$^+$ (80), 263 [278 - Me]$^+$ (40), 201 (42), 183 (90), 108 (52), 71 [RCO]$^+$ (12); HPLC: MeOH-H_2O, 3 : 2, R_t 8.2 min.

3ß-Hydroxy-8α-isobutyryloxy-1-oxo-germacra-4E,10(14)-11(13)-trien-12,6α-olide (11). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3420 (OH), 1780 (γ-lactone), 1735 (CO_2R); MS m/z (rel. int.): 260.105 [M - RCO_2H]$^+$ (2.5) (calc. for $C_{15}H_{16}O_4$: 260.105), 242 [260 - H_2O]$^+$ (2), 204 (10), 91 (30), 71 [RCO]$^+$ (100); HPLC: MeOH-H_2O, 3 : 2, R_t 11.7 min.

3ß-Hydroxy-8ß-angeloyloxygermacra-1(10)E,4E,11(13)-trien-12,6ß-olide (18). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3600 (OH), 1775 (γ-lactone), 1730 (C=CCO_2R); MS m/z (rel. int.): 246 [M - RCO_2H]$^+$ (12), 228 [246 - H_2O]$^+$ (100); HPLC: MeOH-H_2O, 7 : 3, R_t 5.8 min.

3α-Acetoxy-8ß-[3-acetoxy-2-hydroxy-2-methylbutyryloxy]-germacra-1(10)E,4E,11(13)-trien-12,6ß-olide (21). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3600 (OH), 1790 (γ-lactone), 1760, 1250 (OAc), 1730 (CO_2R); MS m/z (rel. int.): 464.204 [M]$^+$ (2) (calc. for $C_{24}H_{32}O_9$: 464.204), 404 [M - HOAc]$^+$ (4), 389 [404 - Me]$^+$ (5), 246 (60), 131 (100), 55 (100); HPLC: MeOH-H_2O, 7 : 3, R_t 4.6 min.

6α-Hydroxy-11αH-germacra-1(10)E,4E-dien-12,8α-olide (25). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3460 (OH), 1790 (γ-lactone); MS m/z (rel. int.): 250.157 [M]$^+$ (12) (calc. for $C_{15}H_{22}O_3$: 250.157), 232 [M - H_2O]$^+$ (8), 217 [232 - Me]$^+$ (6), 109 (100), 81 (90); TLC: Et_2O-petrol, 3 : 2, R_f 0.21.

6α-Tigloyloxy-4α,5ß-epoxygermacr-1(10)E,11(13)-dien-12,8α-olide (26). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1780 (γ-lactone), 1725, 1650 (C=CCO$_2$R); MS m/z (rel. int.): 346 [M]$^+$ (0.1), 246.126 [M - RCO_2H]$^+$ (2) (calc. for $C_{15}H_{18}O_3$: 246.126), 188 (6), 83 [RCO]$^+$ (100), 55 [83 - CO]$^+$ (84); HPLC: MeOH-H_2O, 13 : 7, R_t 13.7 min.

6α-Hydroxy-4α,5ß-epoxy-11αH-germacr-1(10)E-en-12,8α-olide (27). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3600 (OH), 1800 (γ-lactone); MS m/z (rel. int.): 266.152 [M]$^+$ (12) (calc. for $C_{15}H_{22}O_4$: 266.152), 248 [M - H_2O]$^+$ (45), 233 [248 - Me]$^+$ (12), 103 (68), 79 (100), 63 (76); TLC: Et_2O-petrol, 3 : 1, R_f 0.25.

8α-Angeloyloxy-5αH-guaia-1(10),3,11(13)-trien-12,6α-olide (38). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1770 (γ-lactone), 1730 (C=CCO$_2$R); MS m/z (rel. int.): 328.167 [M]$^+$ (calc. for $C_{20}H_{24}O_4$: 328.167), 228 [M - RCO_2H]$^+$ (88), 213 [228 - Me]$^+$ (70), 83 [RCO]$^+$ (100); TLC: Et_2O-petrol, 1 : 4, R_f 0.58.

8α-Angeloyloxy-4α-hydroxy-5αH-guaia-1(10),3,11(13)-trien-12,6α-olide (40). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3500 (OH), 1775 (γ-lactone), 1715 (C=CCO$_2$R); CIMS m/z (rel. int.): 345 [M + 1]$^+$ (5), 327 [345 - H_2O]$^+$ (7), 227 [327 - AngOH]$^+$ (12), 56 (100); HPLC: MeOH-H_2O, 7 : 3, R_t 9.3 min.

8α-Angeloyloxy-4ß-hydroxy-5αH-guaia-1(10),3,11(13)-trien-12,6 - olide (41). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3420 (OH), 1775 (γ-lactone), 1720 (C=CCO$_2$R); CIMS m/z (rel. int.): 327 [M - H$_2$O + 1]$^+$ (0.2), 227 [327 - AngOH]$^+$ (12), 100 [RCO$_2$H]$^+$ (90), 56 (100); TLC: Et$_2$O-petrol, 7 : 3, 3 x, R$_f$ 0.54.

4ß-Hydroperoxy-9α-methoxy-5αH-guaia-1(10),3,11(13)-trien-12,6α-olide (42). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3500 (OH), 1780 (γ-lactone); CIMS m/z (rel.i nt.): 293 [M + 1]$^+$ (20), 278 (100), 275 (45), 261 (30), 227 (26), 89 (70), 73 (100); HPLC: MeOH-H$_2$O, 3 : 2, R$_t$ 8.7 min.

5αH-Guaia-1(10),2,4(15)-trien-12,6α-olide (43). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1780 (γ-lactone); MS m/z (rel. int.): 228.115 [M]$^+$ (100), 213 [M - Me]$^+$ (8), 131 (50), 91 (48); TLC: CH$_2$Cl$_2$, R$_f$ 0.52.

14-Acetoxy-4ß-hydroxy-5αH-guaia-1(10),2-dien-12,6α-olide (44). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3420 (OH), 1790 (γ-lactone), 1745, 1250 (OAc); MS m/z (rel. int.): 306.147 [M]$^+$ (20) (calc. for C$_{17}$H$_{22}$O$_5$: 306.147), 291 [M - Me]$^+$ (38), 246 [M - HOAc]$^+$ (100), 91 (56), 55 (84); HPLC: MeOH-H$_2$O, 3 : 2, R$_t$ 8.7 min.

1α-Hydroperoxy-5αH-guaia-3,9,11(13)-trien-12,6α-olide (45). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3400 (OOH), 1780 (γ-lactone); CIMS m/z (rel.int.): 263 [M + 1]$^+$ (20), 245 (32), 229 (48), 89 (80), 87 (100), 73 (64); HPLC: MeOH-H$_2$O, 3 : 2, R$_t$ 13.0 min.

1α,4α-Endoperoxy-5αH-guaia-2,9,11(13)-trien-12,6α- olide (47). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1780 (γ-lactone); MS m/z (rel. int.): 260.194 $[M]^+$ (6) (calc. for $C_{15}H_{16}O_4$: 260.104), 228 $[M - O_2]^+$ (100), 213 $[228 - Me]^+$ (56), 121 (48), 91 (42); TLC: CH_2Cl_2-Et_2O, 4 : 1, R_f 0.22.

1α,4α-Endoperoxy-5α,11αH-guaia-2,9-dien-12,6α-olide (48). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1790 (γ-lactone); MS m/z (rel.int.). 262.121 $[M]^+$ (6) (calc. for $C_{15}H_{18}O_4$: 262.121), 247 $[M - Me]^+$ (20), 169 (60), 107 (70), 95 (70), 57 (80), 55 (100); HPLC: MeOH-H_2O, 3 : 2, R_t 10.3 min.

10α-Hydroxy-9α-[isovaleryloxy and 2-methylbutyryloxy]-1α,4α-endoperoxyguaia-2,11(13)-dien-12,6α-olide (49/50). Still containing 51; IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1735 (CO_2R); MS m/z (rel. int.): 378 $[M]^+$ (0.5), 346.178 $[M - O_2]^+$ (4) (calc. for $C_{20}H_{26}O_5$: 346.178), 244 $[246 - RCO_2H]^+$ (33), 85 $[RCO]^+$ (95), 57 $[85 - CO]^+$ (100); HPLC: MeOH-H_2O, 7 : 3, R_t 8.5 min.

10α-Hydroxy-9α-isobutyryloxy-1α,4α-endoperoxyguaia-2,11(13)-dien-12,6 -olide (52). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1780 (γ-lactone), 1735 (CO_2R); MS m/z (rel.int.): 362 $[M]^+$ (0.5), 332 $[M - O_2]^+$ (3), 244 $[332 - RCO_2H]^+$ (30), 71 $[RCO]^+$ (100); HPLC: MeOH-H_2O, 7 : 3, R_t 6.7 min.

4Β-10Β-Dihydroxy-1α-methoxy-5α,11αH-guaia-2-en-12,6α-olide (53). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3430 (OH), 1780 (γ-lactone); MS m/z (rel. int.): 296.162 $[M]^+$ (2) (calc. for $C_{16}H_{24}O_5$: 296.162), 278 [M -

$H_2O]^+$ (40), 169 (100), 111 (64), 55 (58); HPLC: MeOH-H_2O, 3 : 2, R_t 9.3 min.

5α-Hydroxy-2α-methoxy-11αH-guaia-1(10),2-dien-12,6α-olide (54). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3450 (OH), 1765 (γ-lactone); MS m/z (rel.int.): 278.152 $[M]^+$ (30) (calc. for $C_{16}H_{22}O_4$: 278.152), 263 $[M - Me]^+$ (12), 173 (38), 153 (96), 125 (80), 69 (64), 57 (100); TLC: CH_2Cl_2-MeOH, 19 : 1, R_f 0.51).

5α-Hydroxy-2-oxo-11αH-guaia-1(10),2-dien-12,6α-olide (55). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3525 (OH), 1760 (γ-lactone), 1675 (C=CC=O); MS m/z (rel.int.): 262.121 $[M]^+$ (90) (calc. for $C_{15}H_{18}O_4$: 262.121), 247 $[M - Me]^+$ (7), 244 $[M - H_2O]^+$ (14), 189 (56), 151 (50), 123 (72), 85 (88), 55 (100); HPLC: MeOH-H_2O, 3 : 2, R_t 5.8 min.

1α,5α-Dihydroxy-11αH-guaia-3,10(14)-dien-12,6α-olide (56). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3530 (OH), 1780 (γ-lactone); MS m/z (rel.int.): 264.136 $[M]^+$ (28) (calc. for $C_{15}H_{20}O_4$: 264.136), 246 $[M - H_2O]^+$ (42), 228 $[246 - H_2O]^+$ (50), 191 (60), 172 (72), 73 (82), 61 (100); HPLC: MeOH-H_2O, 3 : 2, R_t 13.2 min.

1α,5α,3α,4α-Bisepoxy-10ß-methoxy-11αH-guaian-12,6α-olide (57). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 1778 (γ-lactone); MS m/z (rel. int.): 294.146 $[M]^+$ (3) (calc. for $C_{16}H_{22}O_5$: 294.146), 279 $[M - Me]^+$ (7), 220 (42), 153 (50), 85 (100); HPLC: MeOH-H_2O, 3 : 2, R_t 6.6 min.

4ß,5ß-Epoxy-3ß-hydroxy-10α-methoxy-11αH-guaia-1-en-12,6ß-olide (61). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3500 (OH), 1760 (γ-lactone); CIMS m/z (rel.int.): 295 [M + 1]$^+$ (14), 277 (60), 263 (80), 245 (100), 235 (40), 227 (22), 87 (12); HPLC: MeOH-H_2O, 3 : 2, R_t 5.4 min.

3ß,4ß-Dihydroxy-2α,10α-dimethoxy-11αH-guaia-1(5)-en-12,6ß-olide (62). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3460 (OH), 1770 (γ-lactone); MS m/z (rel.int.): 326.172 [M]$^+$ (4) (calc. for $C_{17}H_{26}O_6$: 326.172), 294 [M - MeOH]$^+$ (54), 253 (100), 147 (50), 85 (48), 61 (58), 55 (66); HPLC: MeOH-H_2O, 3 : 2, R_t 7.2 min.

1ß,4α,8α-Trihydroxy-eudesm-11(13)-en-12,6α-olide (70). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3600 (OH), 1765 (γ-lactone); MS m/z (rel. int.): 267.123 [M - Me]$^+$ (28) (calc. for $C_{14}H_{19}O_5$: 267.123), 249 [267 - H_2O]$^+$ (37), 231 [249 - Me]$^+$ (12), 188 (42), 164 (64), 95 (71), 83 (82), 55 (100); ^{1}H NMR ($CDCl_3$): δ 3.33 (dd, H-1), 1.86 (d, H-5), 4.61 (t, H-6), 2.80 (dq, H-7), 4.53 (q, H-8), 2.18 (dd, H-9), 1.46 (br d, H-9'), 6.14 and 5.59 (d, H-13), 1.18 (s, H-14), 1.39 (s, H-15); J [Hz]: 1,2 = 10; 1,2' = 5; 5,6 = 6,7 = 11; 7,8 = 7,13 = 8,9 = 8,9' ~ 3; 9,9' = 14; TLC: Et_2O-MeOH, 19 : 1, R_f 0.55.

5-Oxo-jasoniolide (71). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1788 (γ-lactone), 1720 (C=O); MS m/z (rel.int.): 246.125 [M]$^+$ (10) (calc. for $C_{15}H_{18}O_3$), 231 [M - Me]$^+$ (8), 203 [231 - CO]$^+$ (20), 153 (32), 95 (100), 79 (80), 55 (78); TLC: Et_2O-petrol, 4 : 1, R_f 0.41.

Methyl-5α-hydroperoxy-6ß-hydroxycostoate (75). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3440 (OH), 1710 (C=CCO$_2$R); MS m/z (rel.int.): 296 [M]$^+$ (6), 264 [M - MeOH]$^+$ (5), 246 [264 - H$_2$O]$^+$ (30), 231 [264 - O$_2$H]$^+$ (60), 196 (68), 109 (96), 95 (100), 55 (98); HPLC: MeOH-H$_2$O, 4 : 1, R$_t$ 5.7 min.

Methyl-5ß-hydroperoxycostoate (77). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3400 (OH), 1725 (C=CCO$_2$R); MS m/z (rel.int.): 247 [M - O$_2$H]$^+$ (58), 232 (38), 215 [247 - MeOH]$^+$ (30), 187 (42), 161 (42), 95 (100); HPLC: MeOH-H$_2$O, 3 : 1, R$_t$ 16.8 min.

Methyl-6ß-hydroxy-isocostoate (78). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3480 (OH), 1725 (C=CCO$_2$R); MS m/z (rel.int.): 264.172 [M]$^+$ (10) (calc. for C$_{16}$H$_{24}$O$_3$: 264.172), 246 [M - H$_2$O]$^+$ (16), 232 [M - MeOH]$^+$ (30), 217 [232 - Me]$^+$ (100), 95 (68), 81 (68), 55 (98); HPLC: MeOH-H$_2$O, 4 : 1, R$_t$ 8.3 min.

Methyl-4,5-dioxo-seco-isocostoate (79). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1735 (C=O), 1720 (C=CCO$_2$R); MS m/z (rel. int.): 280.167 [M]$^+$ (10) (calc. for C$_{16}$H$_{24}$O$_4$: 280.167), 248 [M - MeOH]$^+$ (10), 206 (44), 196 [C$_{11}$H$_{16}$O$_3$]$^+$ (100), 164 [196 - MeOH]$^+$ (78); HPLC: MeOH-H$_2$O, 13 : 7, R$_t$ 13.7 min.

Methyl-5ß-hydroxy-4-oxo-11(13)-dehydroiphionoate (80). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1725 (C=CCO$_2$R), 1705 (C=O); MS m/z (rel. int.): 248 [M - MeOH]$^+$ (5), 230 [248 - H$_2$O]$^+$ (6), 196 [M - C$_5$H$_8$O]$^+$ (100), 164 [196 - MeOH]$^+$ (60), 55 (100); HPLC: MeOH-H$_2$O, 13 : 7, R$_t$ 16.4 min.

4ß,5ß-Dihydroxy-10-epi-eudesmane (81). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3600 (OH); MS m/z (rel. int.): 240.208 $[M]^+$ (3.5) (calc. for $C_{15}H_{28}O_2$: 240.208), 222 $[M - H_2O]^+$ (36), 204 $[222 - H_2O]^+$ (24), 197 $[M - C_3H_7]^+$ (88), 179 $[197 - H_2O]^+$ (72), 161 $[179 - H_2O]^+$ (100), 109 (98), 84 (97); HPLC: MeOH-H_2O, 17 : 3, R_t 10.4 min.

4ß,11-Dihydroxy-10-epi-eudesmane (82). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3610 (OH); MS m/z (rel. int.): 222.198 $[M - H_2O]^+$ (2.5) (calc. for $C_{15}H_{26}O$: 222.198), 204 $[222 - H_2O]^+$ (40), 189 $[204 - Me]^+$ (22), 164 (50), 149 (100), 109 (57); HPLC: MeOH-H_2O, 13 : 7, R_t 15 min.

10-epi-Eudesma-3,5-diene (83). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1635 (C=C); MS m/z (rel. i nt.): 204.188 $[M]^+$ (58) (calc. for $C_{15}H_{24}$: 204.188), 189 $[M - Me]^+$ (22), 161 $[M - C_3H_7]^+$ (100), 105 (43), 81 (41); TLC: petrol, R_t 0.75.

2α,4ß-Dihydroxy-5-epi-eremophil-1(10)-ene (84). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3600 (OH); MS m/z (rel. int.): 238.193 $[M]^+$ (9) (calc. for $C_{15}H_{26}O_2$: 238.193), 220 $[M - H_2O]^+$ (82), 205 $[220 - Me]^+$ (100), 177 $[220 - C_3H_7]^+$ (76), 149 (77), 121 (96), 95 (80); HPLC: MeOH-H_2O, 13 : 7, R_t 13 min.

4ß-Hydroxy-5-epi-eremophil-1(19)-en-2-one (85). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3600 (OH), 1715, 1670 (C=CC=O); MS m/z (rel. int.): 236.178 $[M]^+$ (34) (calc. for $C_{15}H_{24}O_2$: 236.178), 221 $[M - Me]^+$ (12), 218 $[M - H_2O]^+$ (14), 178 $[221 - C_3H_7]^+$ (100), 135 (56), 108 (62); CD (MeCN): $\Delta\varepsilon_{345}$ -0.33, $\Delta\varepsilon_{332}$ -0.41, $\Delta\varepsilon_{320}$ -0.34; HPLC: MeOH-H_2O, 13 : 7, R_t 11.6 min.

2α,8α,11-Trihydroxy-5-epi-eremophil-1(10)-ene (86). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3420 (OH); MS m/z (rel. int.): 236.178 [M - H_2O]$^+$ (24) (calc. for $C_{15}H_{24}O_2$: 236.178), 218 [236 - H_2O]$^+$ (10), 178 (44), 149 (98), 124 (100), 109 (94), 81 (62); HPLC: MeOH-H_2O, 13 : 7, R_t 6.4 min.

8α,11-Dihydroxy-5-epi-eremophil-1(10)-en-2-one (87). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3400 (OH), 1700, 1650 (C=CC=O); MS m/z (rel. int.): 252.173 [M]$^+$ (2.5) (calc. for $C_{15}H_{24}O_3$: 252.173), 234 [252 - H_2O]$^+$ (6), 219 [234 - Me]$^+$ (19), 176 (100), 161 (66), 134 (83), 109 (72), 95 (66); CD (MeCN): $\Delta\varepsilon_{347}$ -0.35, $\Delta\varepsilon_{334}$ -0.52, $\Delta\varepsilon_{323}$ -0.47; HPLC: MeOH-H_2O, 13 : 7, R_t 5.7 min.

5-Isovaleryloxydehydrolasiospermane (89). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1735 (CO_2R); MS m/z (rel. int.): 330.183 [M]$^+$ (0.3) (calc. for $C_{20}H_{26}O_4$: 330.183), 228 [M - RCO_2H]$^+$ (40), 213 [228 - Me]$^+$ (2), 165 (22), 147 (42), 85 [RCO]$^+$ (100), 57 [85 - CO]$^+$ (90); TLC: Et_2O-petrol, 1 : 9, R_f 0.62.

8-Acetoxy-12-hydroxyfarnesol (93). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3600 (OH), 1740 (OAc); MS m/z (rel. int.): 278.188 [M - H_2O]$^+$ (0.3) (calc. for $C_{17}H_{26}O_3$: 278.188), 218 [278 - HOAc]$^+$ (1), 203 [218 - Me]$^+$ (1), 150 (20), 123 (26), 93 (100), 68 (78); HPLC: MeOH-H_2O, 7 : 3, R_t 5.8 min.

8-Acetoxy-12-hydroxyfarnesyl acetate (94). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3600 (OH), 1745 (OAc); MS m/z (rel. int.): 278.188 [M - HOAc]$^+$ (0.2) (calc. for $C_{17}H_{26}O_3$: 278.188), 218 [278 - HOAc]$^+$ (2), 200 [218 - H_2O]$^+$ (1), 193 (7), 93 (100); HPLC: MeOH-H_2O, 7 : 3, R_t 12.2 min.

8,12-Dihydroxyfarnesyl acetate (95). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3600 (OH), 1740 (OAc); CIMS m/z (rel. int.): 297 [M + 1]$^+$ (3), 279 [297 - H_2O]$^+$ (0.5), 261 [279 - H_2O]$^+$ (1.5), 219 [279 - HOAc]$^+$ (3), 94 (100); HPLC: MeOH-H_2O, 7 : 3, R_t 6.2 min.

12-Acetoxy-8-hydroxyfarnesol (96). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3600 (OH), 1745 (OAc); CIMS m/z (rel. int.): 297 [M + 1]$^+$ (5), 279 [297 - H_2O]$^+$ (2), 261 [278 - H_2O]$^+$ (8), 219 [279 - HOAc]$^+$ (4), 124 (34), 94 (100); TLC: Et_2O, 3 x, R_f 0.57.

12-Acetoxy-8-hydroxyfarnesyl acetate (97). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3450 (OH), 1750 (OAc); MS m/z (rel. int.): 278.188 [M - HOAc]$^+$ (2) (calc. for $C_{17}H_{26}O_3$: 278.188), 218 [278 - HOAc]$^+$ (4), 200 [218 - H_2O]$^+$ (5), 193 (34), 93 (100); HPLC: MeOH-H_2O, 7 : 3, R_t 11.5 min.

8,12-Diacetoxyfarnesol (98). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 3500 (OH), 1750 (OAc); MS m/z (rel. int.): 278.188 [M - HOAc]$^+$ (4) (calc. for $C_{17}H_{26}O_3$: 278.188), 218 [278 - HOAc]$^+$ (7), 200 [218 - H_2O]$^+$ (6), 193 (22), 151 (44), 123 (54), 43 (100); HPLC: MeOH-H_2O, 7 : 3, R_t 11.6 min.

8,12-Diacetoxyfarnesyl acetate (99). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1750 (OAc); MS m/z (rel. int.): 380.219 $[M]^+$ (0.2) (calc. for $C_{21}H_{32}O_6$: 380.219), 320 $[M - HOAc]^+$ (0.6), 260 $[320 - HOAc]^+$ (2), 200 $[260 - HOAc]^+$ (2), 151 (30), 133 (40), 93 (100); TLC: Et_2O-petrol, 1 : 1, 3 x, R_f 0.56.

8-Acetoxynerolidol (100). IR $\nu_{max}^{CHCl_3}$,cm^{-1}: 3600 (OH), 1735, 1250 (OAc); MS m/z (rel. int.): 220.183 $[M - HOAc]^+$ (4) (calc. for $C_{15}H_{24}O$: 220.183), 202 $[220 - H_2O]^+$ (3), 151 (93), 123 (52), 93 (98), 81 (100), 69 (66); ^{1}H NMR ($CDCl_3$): δ 5.96 (dd, H-1c), 5.20 (dd, H-1t), 5.90 (dd, H-2), 1.55 (m, H-4), 2.05 (m, H-5), 5.42 (br t, H-6), 5.06 (br t, H-8), 2.34 and 2.23 (br ddd, H-9), 4.98 (tqq, H-10), 1.67 (br s, H-12), 1.59 (br s, H-13), 1.60 (br s, H-14), 1.28 (s, H-15), 2.02 (s, OAc); J [Hz]: 1c,2 = 11; 1t,2 = 17.5; 5,6 = 8,9 = 9,10 = 7; 9,9' = 14; 10,12 = 10,13 = 1; TLC: Et_2O-petrol, 1 : 1, R_f 0.55.

Deca-4,6,8-triyn-2E-enol senecioate (103). IR $\nu_{max}^{CCl_4}$,cm^{-1}: 1730 (CO_2R); MS m/z (rel. int.): 163 (2), 147 (4), 126 $[M - RCO_2H]^+$ (1), 83 $[RCO]^+$ (100); HPLC: MeOH-H_2O, 9 : 1, R_t 6.0 min.

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Table 1. ^{1}H NMR spectral data of compounds 6, 8 - 12, 18, 21 and 25 - 27 ($CDCl_3$, 400 MHz, δ-values)

H	6	8	9	10	11	18	21	25	26	27
1	4.42 br d	5.23 br dd	4.09 br t	4.19 br d	-	5.27 m	5.09 m	4.88 br dd	5.35 br dd	5.24 br d
2	2.12 m	2.21 m	2.13 m	2.25 ddd	2.97 m	2.22 m	2.23 m	2.21 m	2.33 m	2.40 dddd
2'	2.00 m	2.40 dddd		2.03 ddd	3.08 br dd	2.44 m	2.50 ddd	2.24 m		2.40 dddd
3	3.76 m	1.20 ddd 2.14 ddd	4.33 d	4.36 br dd	4.60 m	4.51 t	4.99 dd	1.93 m 2.21 m	2.13 ddd 1.28 br ddd	1.20 ddd 2.14 ddd
5	4.29 br d	2.66 d	5.37 br d	5.39 br d	5.16 br d	5.37 m	5.56 br d	4.67 br d	2.77 d	2.76 d
6	4.35 t	3.90 t	4.51 t	4.59 t	4.65 t	5.41 dd	5.38 dd	4.35 ddd	4.92 dd	3.47 dd
7	2.47 dddd	2.18 ddd	3.35 dddd	3.21 dddd	2.97 m	3.40 m	3.39 m	2.37 ddd	3.17 dddd	2.51 ddd
8	4.79 br dd	3.82 dddd	5.24 ddd	5.15 br dd	4.82 br ddd	5.37 m	5.34 m	4.39 ddd	4.14 ddd	4.40 ddd
9	2.01 dd	2.45 m	2.46 br dd	2.32 dd	2.79 dd	2.79 br d	2.70 br d	2.37 dd	2.24 br dd	2.41 dd
9'	2.32 br d		2.32 br dd	2.51 br d	2.58 br d	2.39 dd	2.39 dd	2.87 br d	2.72 br d	2.84 br d
11	-	2.90 dq	-	-	-	-	-	2.92 dq	-	2.99 dq
13	6.44 dd	1.44 d	6.23 d	6.25 d	6.28 dd	6.39 d	6.40 d	1.42 d	6.33 d	1.41 d
13'	5.65 br d		5.62 d	5.69 d	5.75 dd	5.81 br s	5.78 d		5.76 d	
14	1.27 br s	1.75 br s	5.35 t 5.26 t	5.50 br s 5.30 d	5.94 d 5.88 br s	1.51 br s	1.41 br s	1.44 br s	1.81 br s	1.27 s
15	1.35 d	1.27 s	1.80 d	1.73 br s	1.80 d	1.73 br s	1.72 br s	1.64 br s	1.31 s	1.73 br s
OCOR	2.28 qq	-	2.60 qq	2.60 qq	2.59 qq	6.11 qq	4.89 q	-	6.93 qq	-
	1.01 d	-	1.22 d	1.22 d	1.20 d 1.23 d	1.99 dq	1.15 br d		1.79 br d	
						1.91 dq	1.49 br s		1.83 br s	
OH	-	1.56 d		7.80 br s			2.12 s	1.13 q		2.07 br s

J[Hz]: Compound 6: 1,2' = 11; 1,14 = 5,15 = 1; 5,6 = 6,7 = 10; 7,8 = 8,9 = 9; 7,13 = 3.5; 7,13' = 3; 9,9' = 12; 13,13' = 0.5; compound 8: 1,2 = 4; 1,2' = 13; 1,14 = 1; 2,2' = 13; 2,3 = 5; 2,3' = 2; 2',3 = 13; 2',3' = 5; 3,3' = 13; 5,6 = 6,7 = 9; 7,8 = 8; 7,11 = 11; 8,9 = 9; 8,9' = 4; 8,OH = 5; 11,13 = 7; compounds 9 - 11: 5,6 = 6,7 = 7,8 = 10; 5,15 = 1.5; 7,13 = 3.5; 7,13' = 3; 9,14 = 1 (compound 9: 1,2 = 1,2' =2,3 = 6.5; 8,9 = 6; 8,9' = 2.5; 9,9' = 14; compound 10: 1,2 = 2,3 = 3; 1,2' = 11; 2,2' = 13; 2',3 = 11; 8,9 = 8; 8,9' = 1.5; 9,9' = 17; compound 11: 2,2' = 2',3 = 11; 8,9 = 10; 8,9' = 2; 9,9' = 14; 13,13' = 0.5); compound 18: 1,14 = 1.5; 2,3 = 2',3 = 3; 5,6 = 11; 5,14 = 1.5; 6,7 = 7; 7,8 = 1; 7,13 = 7,13' = 2; 8,9' = 4.5; 9,9' = 14; compound 21: 1,2 = 11; 1,2' = 2',3 = 5; 1,14 = 5,15 = 1; 2,2' = 12; 2,3 = 5,6 = 11; 6,7 = 7; 7,8 = 1; 7,13 = 7,13' = 2; 8,9 = 2; 8,9' = 5; 9,9' = 15; 18,19 = 7; compound 25: 1,2 = 4; 1,2' = 12; 5,6 = 6,7 = 10; 5,15 = 1; 6,OH = 3; 7,8 = 10.5; 7,11 = 7.5; 8,9 = 11; 8,9' = 2; 9,9' = 12; 11,13 = 7.5; compound 26: 1,2 = 1,2'~ 8; 2,3 = 2',3 = 4; 2,3' = 2',3'~ 9; 3,3' = 9,9' = 13; 5,6 = 6,7 = 9; 7,8 =4.5; 7,13 = 3; 7,13' =2.7; 8,9 = 11; 8,9' =2; OTigl: 3',4' = 7; compound 27: 1,2 = 2; 1,2' = 2,2' = 13; 2,3 = 6; 2,3' = 2; 2',3 = 13; 2',3' = 5; 3,3' = 13; 5,6 = 9; 5,15 = 1; 6,7 = 7,8 = 10; 7,11 = 7.5; 8,9 = 11; 8,9' = 1.5; 9,9' = 13; 11,13 = 7.5; OiBu: 2',3' = 2',4' = 7; OAng: 3',4' = 7; 3',5' = 4',5' =1.5.

Table 2. ^{1}H NMR spectral data of compounds 38 and 40 - 45 (400 MHz, $CDCl_3$, δ-values)

H	38	40	41	42*	43	44	45+
2	2.95 br d	6.33 d	6.46 d	6.64 d	6.35 br d	6.56 d	2.53 ddq
2'	3.03 br d						2.60 ddq
3	5.57 m	5.95 d	5.92 d	5.98 d	6.58 dd	6.02 br d	5.44 br s
5	3.39 br d	3.04 br d	2.78 br d	3.05 dq	3.56 br d	2.76 br d	3.25 br d
6	3.73 dd	4.11 dd	4.19 dd	4.23 dd	3.61 t	4.34 t	4.00 dd
7	3.22 dddd	3.18 dddd	3.24 dddd	3.37 m	2.84 m	2.34 dddd	3.13 m
8	4.96 ddd	5.12 ddd	5.03 ddd	2.46 ddd 1.56 m	2.14 dddd 1.35 dddd	1.84 dddd 1.40 dddd	2.74 dddq 2.11 dddq
9	2.54 br dd	2.53 m	2.52 br dd	3.87 dd	2.37 br ddd	2.23 br ddd	5.71 m
9'	2.34 dd		2.46 dd		2.26 ddd	2.45 ddd	
11	-	-	-	-	-	2.71 dq	-
13	6.14 d	6.26 d	6.22 d	6.18 d	6.14 d	1.19 d	6.24 d
13'	5.55 d	5.75 d	5.69 d	5.44 d	5.42 d		5.51 d
14	1.78 br d	1.87 d	1.91 br s	2.00 d	1.92 br s	4.69 br d 4.63 br d	1.88 br s
15	1.95 br	1.46 s	1.59 s	1.57 s	5.26 br s 5.15 br s	1.58 s	1.94 br s
OCOR	6.19 qq	6.22 qq	6.21 qq	-	-	2.06 s	
	2.03 dq	2.03 dq	2.03 dq				
	1.91 dq	1.93 dq	1.92 dq				

*) OOH 8.01 s, OH 3.34 s; +) OOH 7.47 s.

J[Hz]: Compound 38: 2,2' = 20; 2,14 = 2',14 = 2,15 = 2',15 = 3,14 ~ 1; 5,6 = 6,7 = 7,8 = 10; 7,13 = 7,13' ~ 3; 8,9 = 10; 8,9' = 2; 9,9' = 13.5; OAng: 3',4' = 7; 3',5' = 4',5' = 1.5; compounds 40 and 41: 2,3 = 6; 5,6 = 6,7 = 7,8 = 10; 7,13 ~ 7,13' = 3; 8,9 = 10; 8,9' = 3; 9,9' = 15; 9,14 = 2; compound 42: 2,3 = 6; 5,6 = 6,7 = 10.5; 7,13 = 7,13' ~ 3; 5,14 = 8',9 = 1.5; 7,8 = 2.5; 8,8' = 14; 8,9 = 5.5; compound 43: 2,3 = 6; 2,14 = 3,15 = 2; 5,6 = 6,7 = 10; 5,14 = 5,15 = 5,15' = 9,14 ~ 1; 7,8 = 3; 7,8' = 8,8' = 13; 7,13 = 7,13' ~ 3; 8,9 = 3; 8,9' = 6; 9,9' = 15; compound 45: 2,2' = 18; 2.3 = 2,3' = 2,15 = 2'15 = 3,15 ~ 2; 5,6 = 11; 6,7 = 9; 7,8 = 5; 7,8' = 12; 7,13 = 3.5; 7,13' = 3; 8,8' = 18; 8,14 = 1.5; 8,9 = 8,14 = 2.5; 9,14 = 1.

Table 3. ^{1}H NMR spectral data of compounds 47, 48, 49, 50 and 52 - 57 (400 MHz, $CDCl_3$, δ-values)

H	47	48	49/50*	52+	53++	54°	55	56	57
2	6.22 d	6.21 d	6.41 br d	6.41 br d	5.72 d	4.70 br s	-	2.83 br dq	2.03 d
3	6.31 d	6.31 d	6.35 br d	6.36 br d	6.10 d	5.80 dq	6.13 q	2.53 br dq	2.11 dd
5	2.55 d	2.43 d	2.65 br d	2.65 br d	2.32 d	-	-	5.67 br s	3.42 d
6	3.81 t	3.98 t	3.78 dd	3.78 dd	4.86 dd	4.01 d	4.06 d	4.15 d	4.75 d
7	2.75 ddddd	2.32 dddd	3.45 m	3.45 m	2.56 dddd	3.19 dddd	3.22 dddd	2.05 m	2.43 dddd
8	2.62 ddd	2.25 ddd	2.32 m	2.32 ddd	1.62 m	1.78 dddd	1.87 dddd	1.91 dddd	1.42 dddd
8'	2.02 dddd	1.98 dddd	1.95 m	1.95 ddd		1.47 dddd	1.46 dddd	1.36 dddd	1.25 m
9	5.73 ddq	5.69 ddq	5.04 br dd	5.02 br dd	2.32 ddd	2.77 br dd	2.91 ddd	2.65 ddd	1.49 ddd
9'					1.46 ddd	2.00 ddd	2.15 ddd	2.26 ddd	1.86 ddd
11	-	1.64 dq	-	-	2.60 dq	2.64 dq	2.69 dq	2.67 dq	2.64 dq
13	6.21 d	1.14 d	6.18 d	6.18 d	1.20 d	1.13 d	1.14 d	1.16 d	1.18 d
13'	5.48 d		5.43 d	5.45 d					
14	1.89 dd	1.86 dd	1.36 s	1.36 s	1.28 s	1.89 s	2.26 d	5.06 br s	1.29 s
15	1.72 s	1.68 s	1.72 s	1.72 s	1.50 s	1.98 dd	2.40 s	1.82 br d	1.70 s

*) OiVal 2.28 d, 2.15 m, 0.99 d; OMebu 2.47 ddq, 1.20 d, 0.94 t; +) OiBu: 2.66 qq, 1,23 d, 1,22 d; ++) OMe 3.16 s, OH 3.48 br s; °) OMe 3.22 s.

J Hz : Compounds 47 and 48: 2,3 = 5.5; 5,6 = 6,7 = 10; 7,8 = 3; 7,8' = 11; 7,13 = 3.5; 7,13' = 3, 8,8' = 16; 8,9 = 9, 8',9 = 2.5; 8',14 = 9,14 ~ 2.5 (compound 48: 7,11 = 8; 11,13 = 8); compounds 49, 50 and 52: 2,3 = 5.5; 5,6 = 6,7 = 10; 7,8 = 7.5; 7,8' = 11; 7,13 = 3.5; 7,13' = 3; 8,8' = 13.5; 8,9 = 9; 8',9 = 8; compound 53: 2,3 = 6; 5,6 = 9; 6,7 = 10.5; 7,8 = 3; 7,8' = 11; 7,11 = 11,13 = 8; 8,9 = 6; 8',9' = 3.5; 8',9 = 12; 9,9' = 14; compound 54: 2,15 = 3,15 =8,9 = 8',9' ~ 1.5; 6,7 = 11; 7,8 = 3; 7,8' = 12; 7,11 = 11,13 = 8; 8,8' = 13; 8,9' = 6; 8',9 = 13; 9,9' = 14; compound 55: 3,15 = 8,9 = 1; 6,7 = 11; 7,8 = 3; 7,8' = 12; 7,11 = 11,13 = 7.5; 8,8' = 8',9 = 13; 8,9' = 6; 9,9' = 14; compound 56: 2,2' = 16.5; 2,3 = 2,3' = 3,15 = 2; 6,7 = 10.5; 7,8 = 8,9 = 8,9' = 4; 7,8 = 8,8' = 9,9' = 13; 7,11 = 11,13 = 7.5; 9,14 = 1; compound 57: 2,2' = 16; 2',3 = 3; 6,7 = 7,8' = 11; 7,8 = 2; 7,11 = 11,13 = 7.5; 8,8' = 13; 8,9 = 2; 8,9' = 6; 8',9 = 8',9' = 1.5; 9,9' = 15.

Table 4. ^{13}C NMR spectral data of compounds 53, 57, 62, 72a and 100 (100.6 MHz, $CDCl_3$, δ-values)+

C	53	57	62	72a	73a	100
1	76.5	78.6	142.5	145.3	145.4	111.8
2	123.9	28.6	77.1	127.3	127.4	144.8
3	143.1	67.1	89.2	121.2	130.0	73.3
4	94.5	66.3	83.3	135.0	135.2	41.5
5	54.8	61.6	140.5	132.9	133.2	22.4
6	82.3	80.8	77.9	130.3	140.3	128.3
7	40.0	39.4	38.8	39.2	40.2	133.0
8	22.7	19.1	20.5	31.9	30.3	79.2
9	35.8	32.2	35.7	140.2	121.0	31.5
10	79.2	81.3	76.8	134.7	134.4	119.1
11	39.2	42.6	40.5	141.0	43.1	134.1
12	180.5	178.8	178.9	167.0	175.9	25.7
13	10.6	9.9	10.3	126.6	14.5	17.9
14	29.0	17.4	27.8	22.2	22.1	11.9
15	25.8	23.4	23.9	12.4	12.5	27.9
OMe	50.2	48.9	58.1	51.7	52.0	OAc 170.4
			50.1			21.3

+) Some signals may be interchangeable.

Table 5. ^{1}H NMR spectral data of compounds 61, 62, 70 and 71 (400 MHz, $CDCl_3$, δ-values)

H	61	62	70(MeOD)	71
1	-	-	3.33 d	2.03 ddd 1.91 ddd
2	5.76 d	4.05 br s	1.68 m	2.36 m
3	4.38 dd	3.78 br s	1.61 br d 1.74 m	5.56 ddd
5	-	-	1.86 d	-
6	4.80 d	5.20 br d	4.61 t	2.44 ddd 2.71 ddd
7	2.92 dddd	2.93 m	2.80 dq	3.73 ddddd
8	1.82 dddd	1.65 m	4.53 q	4.52 ddd
8'	1.46 m	1.45 m		
9	1.95 ddd	1.97 m	2.18 dd	2.03 dd
9'	1.67 ddd	1.65 m	1.46 br d	1.89 dd
11	2.80 dq	2.85 dq	-	-
13	1.20 d	1.19 d	6.14 d	6.26.d
13'			5.59 d	5.66 d
14	1.33 s	1.33 s	1.18 s	1.14 s
15	1.66 s	1.56 s	1.39 s	3.51 d 3.22 br d
OMe	3.20 s	3.15 s 3.42 s		
OH	1.66 d			

J[Hz]: Compound 61: 2,3 = 8',9' ~ 2.5; 3,OH = 12; 6,7 = 6; 7,8 = 4; 7,8' =10.5; 7,11 = 11,13 = 7; 8,8' = 9,9' = 15; 8,9 = 3.5; 8,9' = 7; 8',9 = 12; compound 62: 2,6 = 0.5; 6,7 = 5.5; 7,11 = 11,13 = 7.5; compound 70: 1,2 = 10; 1,2' = 5; 3,3' =14; 5,6 = 6,7 = 10.5; 7,8 = 7,13' ~ 3; 8,9 = 2.5; 9,9' = 14; compound 71: 1,1' = 14; 1,2 = 5; 1,2' = 7; 1',2 = 5; 1',2' = 10; 2,3 = 2',3 = 3,15' = 2.5; 6,6' = 16.5; 6,7 = 4, 6',7 = 13; 6',15' = 1; 7,8 = 4; 7,13 = 7,13' = 2; 8,9 = 3; 8,9' = 12; 9,9' = 15,15' = 15.

Table 6. ^{1}H NMR spectral data of compounds 72a, 73a, 75 and 77 - 80 (400 MHz, $CDCl_3$, δ-values)

H	72a	73a	75	77	78	79	80
1α	-	-	1.92 ddd	1.19 br d	x	1.50 m	1.48 m
1β	-	-	0.96 br d	1.83 ddd	x		1.90 ddd
2α	6.08 br s	6.08 br s	1.60 m	1.60 m	1.7-1.2 m	1.50 m	2.08 m
2β			1.66 m				1.92 m
3α	6.30 br s	6.30 br s	2.58 ddddd	2.37 ddddd	2.05 m	2.45 m	3.49 m
3β			2.22 br d	2.23 br d	1.97 br dd		
6	6.52 br d	6.63 br d	4.40 br s	2.53 ddd 1.60 m	4.85 br d	2.41 ddd 2.56 dd	1.93 ddd 1.46 dd
7	3.90 m	2.90 m	2.58 br dt	2.80 br dddd	2.67 br dt	2.91 dddd	2.62 br dddd
8α	2.55 br ddd	2.30 m	1.33 br d	1.60 m	1.7-1.2 m	1.90 ddddd	1.63 br dddd
8β	2.46 br ddd		2.02 dddd		2.12 dddd	1.80 dddd	1.32 dddd
9α	5.37 br ddq	5.45 br ddq	1.74 ddd	1.90 ddd	1.7-1.2 m	1.74 m	1.45 m
9β			1.26 ddd	1.04 ddd			
13	6.31 d	1.20 d	6.40 br s	6.19 br s	6.38 br s	6.23 br s	6.17 br s
13'	5.63 d		5.69 br s	5.61 br s	5.73 br s	5.56 br s	5.58 br s
14	1.92 d	1.93 d	1.16 s	1.02 s	1.23 s	1.15 s	1.03 s
15	2.02 d	2.03 d	5.26 t	5.41 t	1.73 br s	2.14 s	2.24 s
15'			5.17 t	5.34 t			
OMe	3.79 s	3.70 s	3.78 s	3.77 s	3.78 s	3.77 s	3.75 s
OOH	-	-	7.97 s	7.67 s	-	-	
OH	-	-	1.43 s	-	-	-	

x) Overlapped multiplets.

J[Hz]: Compounds 72a and 73a: 2,3 = 2,6 = 2,9 = 3,6 = 3,15 ~ 1; 6,7 = 5; 7,8 = 8,9 = 8'9 ~ 7; 7,8' = 3.5; 8,8' = 15; (compound 72a: 7,13 = 7,13' ~ 1; compound 73a: 7,11 = 7); compound 75: 1α,1ß = 1α,2ß = 3α,3ß = 7,8ß = 8α,8ß = 13; 1α,2α = 2α,3α ~ 5; 3α,15 = 3α,15' = 3ß,15 = 3ß,15' ~ 1; 6,7 = 2, 6,OH = 3; 7,8α = 2; 7,13 = 7,13' ~ 1; 8α,9α = 4; 8α,9ß = 3; 8ß,9α = 4; 8α,9ß = 8ß,9ß = 3; 13,13' ~ 1; compound 77: 1α,1ß = 6α,6ß = 14; 1α,2α = 1α,2ß = 1α,3ß = 2; 3α,3ß = 2ß,3α = 13; 2α,3α = 6; 3α,15 = 3α,15' = 3ß,15 = 3ß,15' ~ 1; 6α,7 = 7,8α = 3; 6α,8α = 2; 6ß,7 = 7,8ß = 13; 7,13 = 7,13' = 1; 8α,9ß = 8ß,9ß = 3; 8α,9α = 4.5; 8ß,9α = 9α,9ß = 13; compound 78: 3α,3ß = 17; 2ß,3ß = 6; 6,7 = 2; 7,8ß = 13; 7,13 = 7,13' ~ 1; compound 79: 6α,6ß = 14; 6α,7 = 5; 6ß,7 = 7,8ß = 11; 6α,8α = 2; 7,8α = 4.5; 8α,8ß = 14; 8α,9α = 8α,9ß = 4.5; compound 80: 1α,1ß = 1ß,2α = 12; 1ß,2ß = 6; 6α,6ß = 6ß,7 = 7,8ß = 8α,8ß = 13; 6α,7 = 7,8α = 8α,9α = 8α,9ß ~ 3; 6α,8α = 1.

Table 7. ^{1}H NMR spectral data of compounds 93 - 99 (400 MHz, $CDCl_3$, δ-valuess)

H	93	94	95	96	97	98	99	multipl.
1	4.08	4.54	4.57	4.08	4.57	4.08	4.54	br d
2	5.45	5.36	5.36	5.43	5.36	5.43	5.36	tq
4,5	2.16	2.13	2.15	2.15	2.15	2.13	2.13	br s
6	5.39	5.40	5.39	5.41	5.39	5.40	5.40	tq
8	5.12	5.12	4.02	4.03	4.03	5.10	5.13	t
9	2.42	2.42	2.34	2.34	2.34	2.43	2.43	ddd
9'	2.34	2.31	2.29	2.28	2.29	2.30	2.30	ddd
10	5.27	5.28	5.39	5.45	5.45	5.39	5.33	ttq
12	3.98	3.98	4.02	4.47	4.46	4.43	4.43	br s
13	1.66	1.66	1.69	1.69	1.68	1.66	1.66	d
14	1.62	1.62	1.64	1.63	1.62	1.61	1.62	d
15	1.72	1.76	1.77	1.77	1.77	1.73	1.75	d
OAc	2.04	2.03	2.05	2.08	2.06	2.04	2.04	s
		2.05			2.08	2.07	2.05	s
							2.07	s

J[Hz]: 1,2 = 5,6 = 8,9 = 8,9' = 9,10 = 9',10 = 7; 1,15 = 6,14 = 10,12 = 10,13 ~1; 9,9' = 14.

Table 8. ^{1}H NMR spectral data of compounds 81 - 87 (400 MHz, $CDCl_3$, δ-values)

H	81	82[a)]	83	84[c)]	85	86	87
1	1.67-1.48 m 0.97 m	1.29 m 1.05 m	b)	5.39 ddd	5.85 br s	5.38 ddd	5.72 ddd
2	1.67-1.48 m	1.5-1.4 m	2.27 br m 2.04 br ddd	4.36 dddd	-	4.23 dddd	-
3	1.86 br ddd 1.45 m	1.68 br d 1.40 m	5.51 br d	1.90 ddd 1.66 dd	2.79 d 2.45 dd	1.80 m 1.37 ddd	2.24 dd 2.16 ddd
4	-	-	-	-	-	1.45 m	1.87 ddq
5	-	1.66 dd	-	-	-	-	-
6	1.89 ddd 1.66 dd	2.03 br d 1.33 m	5.56 br d	1.63 dd 1.38 ddd	1.75 br dd 1.61 ddd	1.74 dd 0.70 dd	1.79 dd 0.82 dd
7	1.34 m	1.57 m	1.95 br m	1.30 ddddd	1.50 m	1.80 m	1.84 m
8	1.71 dddd 1.62 m	1.72-1.57 m	a)	1.61 ddddd 0.92 m	1.86 dddd 1.12 m	3.68 ddd	3.71 ddd
9	1.86 br ddd 0.88 ddd	1.50 m 1.08 br d	a)	2.19 ddddd 2.07 ddd	2.52 - 2.42 m	2.42 - 2.30 m	2.50 br d
11	2.01 dqq	-	1.61 dqq	1.40 dqq	1.50 m	-	-
12	0.93 d	1.23 s	0.94 d	0.92 d	0.93 d	1.25 s	1.19 s
13	0.89 d	1.21 s	0.90 d	0.90 d	0.91 d	1.21 s	1.08 s
15	1.27 s	1.02 s	1.78 ddd	1.02 s	1.28 s	0.91 d	0.92 d

a) After addition of $Eu(fod)_3$ H-7 3.09 br t, H-8e 2.78 br d, H-8ax 2.55 br ddd ($J_{6ax,7} = J_{7,8ax} \sim 5$);
b) obscurded; c) in C_6D_6.

J[Hz]: Compound 81: 1,6 = 0.5; 2,3 = 3,3' = 13; 2',3 = 5; 6,6' = 15; 6,7 = 6,8' = 2; 6'7 = 6.5; 7,8 = 5.5; 7,11 = 10.5; 8,8' = 8,9 = 14; 8,9' = 8',9' = 3.5; 6',9 = 5; 9,9' = 13; 11,12 = 11,13 = 7; compound 82: 3,3' = 13; 6,6' = 14; 9,9' = 12; compound 83: 1,2' = 1',2' = 6; 2,2' = 19; 2,3 = 5; 2,15 = 2; 2',15 = 3,15 = 1; 6,7 = 4.5; 7,11 = 11,12 = 11,13 = 7; compound 84: 1,2 = 1,9 = 2,9 = 2; 1,3 = 1; 2,3 = 7, 2,3' = 10; 3,3' = 6,6' = 6,7 = 7,8' = 8,8' = 13; 6',7 = 6',8 = 7,8 = 3; 7,11 = 5; 8,9 = 5; 8,9' = 8',9' = 2.5; 8',9 = 9,9' = 14; 11,12 = 11,13 = 7; compound 85: 1,3' = 1; 3,3' = 17, 6,6' = 6,7 = 8,8' = 13; 6'7, 6',8 = 8,9' = 2.5; 8,9 = 5; 11,12 = 11,13 = 7; compound 86: 1,2 = 1,9 = 2,9 = 2; 1,3 = 1; 2,3 = 7; 2,3' = 10; 3,3' = 3',4 = 12.5; 4,15 = 6.5; 6,6' = 6',7 = 13; 6,7 = 3; 7,8 = 8,9 = 10; 8,9' = 5.5; compound 87: 1,3 = 1,9 = 1; 3,3' = 17; 3,4 = 13; 3'4 = 4.5; 4,15 = 6.5; 6,6' = 6',7 = 13; 6,7 = 3; 7,8 = 10; 8,9 = 8.

Table 9. ^{13}C NMR spectral data of compounds 81 - 83, 85 and 87 (100.6 MHz, $CDCl_3$, δ-values)

C	81[a]	82[a]	83[a]	85[b]	87[b]
1	33.7	41.4	37.1	124.2	125.5
2	19.2	20.1	22.9	197.2	199.5
3	37.0	43.5	124.1	48.9	41.9
4	74.6	77.0	131.2	76.1	40.1
5	78.8	48.5	132.0	44.5	38.9
6	26.0	20.5	123.7	33.2	38.8
7	40.5	41.7	40.7	39.0	48.5
8	22.4	21.3	20.8	28.8	72.3
9	34.7	41.5	35.7	34.3	41.8
10	37.6	34.2	32.3	168.1	167.7
11	29.3	74.6	33.2	32.7	75.1
12	21.9	29.9	20.8	20.0	30.3
13	22.9	29.5	20.7	19.6	23.5
14	22.7	18.4	20.1	22.6	16.9
15	24.0	21.8	23.0	23.1	15.2

a) 2D COSY

b) some signals may be interchangeable.

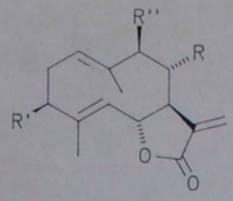
Table 10. Isolated Compounds From the Various Ursinia species

Species (voucher in parenthesis)*	aerial parts	
U. abrotanifolia Spreng (86/183, Cape, Sept. 1986)	95 g	47 mg germacrene D, 9 mg ß-farnesene, 19 mg bicyclogermacrene, 15 mg spathulenol, 150 mg 91, 40 mg laurenobiolide, 16 mg 29, 35 mg 31, 23 mg 32, 14 mg 33, 7 mg 34, 7 mg 35, 16 mg 36; 20 g roots: 8 mg 88, 12 mg 91, 2 mg 92, 1 mg 108, 4 mg coumarin, 3 mg 106
U. anthemoides (L.) Poiret (RMK 9505, NW Australia, Sept. 1986	210 g	5 mg 19, 10 mg 20, 5 mg 21, 93 - 99 (ca. 10 mg each), 2 mg 103
U. cakilefolia DC (86/125, Cape, Sept. 1986)	130 g	10 mg umbelliferone methyl ether, 10 mg 1, 10 mg 14, 10 mg 15, 10 mg 16, 10 mg 17, 2 mg 18, 20 mg 22, 3 mg 38, 2 mg 40, 5 mg 41, 10 mg 63, 30 mg 88, 10 mg 92.
U. dentata (L.) Poir. (86/175, Cape, Sept. 1986)	140 g	10 mg taraxasteryl- and 3 mg lupeylacetate, 20 mg 49 - 52 (ca. 1:1:2:2) 300 mg 100; 85 g roots: 10 mg coumarin, 30 mg 100, 5 mg of a mixture of 49 - 52
U. eckloniana (Sond.) N.E.Br. (86/102 Montagu-Pass, R.S.A., Sept. 1986)	360 g	50 mg cycloartenyl acetate, 10 mg ß-amyrin, 50 mg ß-farnesene, 10 mg 101, 10 mg 102, 30 mg 104, 50 mg 105, 20 mg 64, 20 mg 65, 30 mg 66, 20 mh 67, 4 mg 68, 5 mg 69, 2 mg 71, 8 mg 74, 20 mg 76, 15 mg 77, 10 mg 79, 10 mg 80
U. nana DC (88/31, Namibia, March 1988)	100 g	10 mg caryophyllene, 10 mg α-humulene, 10 mg α-curcumene, 10 mg ϱ-curcumene, 20 mg taraxasteryl acetate, 100 mg umbelliferone methyl ether, 100 mg methyl L caffeoate, 20 mg 88, 70 mg 13, 5 mg 54, 10 mg 55, 2 mg 56, 10 mg 57, 30 mg 59, 1 mg 61, 3 mg 62
U. nudicaulis (Thunb.) N.E.Br. (86/89 Humansdorp, Sept. 1986) RSA	110 g	30 mg caryophyllene, 30 mg germacrene D, 50 mg taraxasteryl acetate, 300 mg 1, 20 mg 2, 340 mg 3, 90 mg 4, 60 mg laurenobiolide, 10 mg 27
(86/139, Viljoens Pass, R.S.A., Sept. 1986)	130 g	5 mg germacrene D, 140 mg taraxasteryl acetate, 20 mg 104, 40 mg 5, 5 mg 37, 20 mg 39, 5 mg 42, 2 mg 43, 5 mg 44, 2 mg 45, 5 mg 47, 5 mg 48, 10 mg 53, 2 mg 72a/73a (crude fraction contained ca. 50 mg 72 and 73 (ca. 1 : 2)), 10 mg 60.

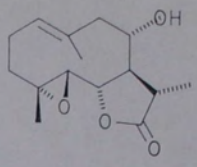
Continuation of Table 10.

U. rigidula (DC) N.E.Br. (86/95, Outeniqua Pass, R.S.A. Sept. 1986)	170 g	20 mg taraxasteryl acetate, 40 mg lupeylacetate, 10 mg sitosterol, 50 mg laurenobiolide, 50 mg 26, 1.5 g 28
U. sericea N.E.Br. (86/124, Cape, Sept. 1986)	225 g	20 mg caryophyllene, 20 mg 88, 27 mg 89, 10 mg isointermedeol, 10 mg 10-epi-γ-eudesmol, 10 mg 2, 5 mg 7, 10 mg 8, 10 mg 12, 50 mg 23, 1 g laurenobiolide, 20 mg 24, 5 mg 25, 5mg 27, 100mg 30
U. speciosa DC (86/188, Muizenberg Slopes, R.S.A., Sept. 1986)	190 g	3 mg caryophyllene, 5 mg ß-farnesene, 2 mg α- and 5 mg γ-curcumene, 5 mg isoaromadendrene, 15 mg benzylbenzoate, 100 mg farnesyl acetate, 5 mg caryophyllenepoxide, 10 mg spathulenol, 5 mg 103, 5 mg 91, 2 g 15 and 4 g 21
U. tenuifolia DC var. tenuifolia (86/114, Swartberg Pass, R.S.A., Sept. 1986)	20 g	30 mg 90, 15 mg 6, 2 mg 9, 2 mg 10, 1 mg 11, 10 mg 75, 3 mg 78
U. trifida Less. (86/97, Outenigua Pass, R.S.A., Sept. 1986)	110 g	35 mg ß-farnesene, 10 mg coumarin, 380 mg 81, 2 g 82, 5 mg 83, 5 mg 84, 10 mg 85, 10 mg 86, 20 mg 87, 5 mg 107, 15 mg 108; 55 g roots: 5 mg 88, 20 mg 108, 200 mg 82,

*) Voucher from the R.S.A. collection are deposited in the Compton Herbarium at Kirstenbosch, that from Australia in the US National Herbarium, Washington, U.S.A. and that from Namibia in the SW African Herbarium at Windhoek.



	1	2	3	4	5	6	7
R	H	OH	H	H	H	OiBu	OH
R'	H	H	H	H	OH	OH	H
R''	H	H	OH	OAc	H	H	H
							1β,10α epoxide



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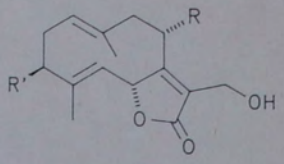
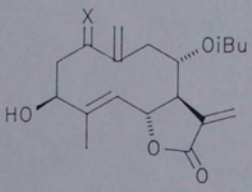
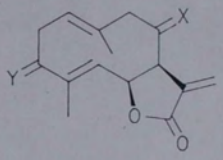


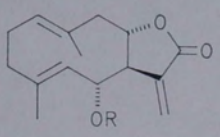
	12	13
R	OH	H
R'	H	OAc



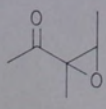
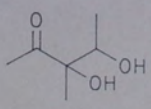
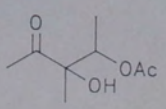
	9	10	11
X	βOH,H	βOOH,H	O

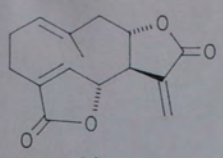


	14	15	16	17	18	19	20	21	22
X	βOA,H	βOA,H	βOA,H	βOB,H	βOAng,H	βOA,H	βOC,H	βOC,H	O
Y	βOH,H	βOAc,H	αOH,H	H_2	βOH,H	H_2	H_2	αOAc,H	H_2



	23	24	25	26	27	28	29
R	Ang	H	H	Tigl	H	H	H
		4β,5α epoxide	11α,13H	4α,5β epoxide	4α,5β epoxide 11α,13H	4α,5β epoxide	1β,10α epoxide

*) A=  ; B=  ; C= 



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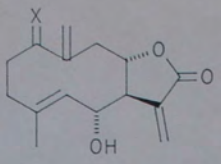
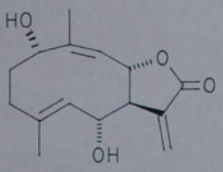


	31	32	33	34	35
X	αOOH,H	βOOH,H	αOH,H	βOH,H	O



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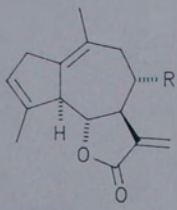
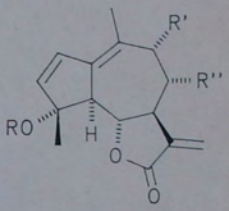
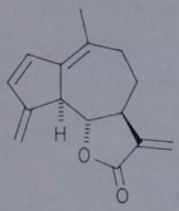


37	38	39
H	OAng	H
		1β,10β epoxide



	40	41	42
R	H	H	OH
R'	H	H	OMe
R''	OAng	OAng	H
	4-epi?	4-epi?	4-epi?



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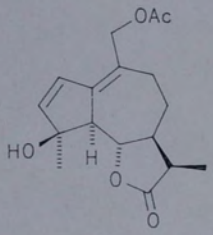

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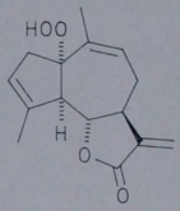

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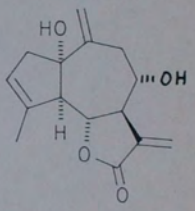

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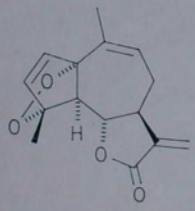
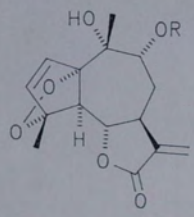
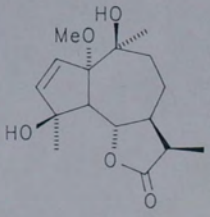


47 48

11α,13 H



	49	50	51	52
R	iVal	Mebu	Ang	iBu



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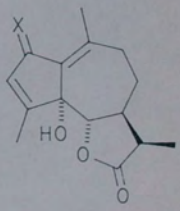
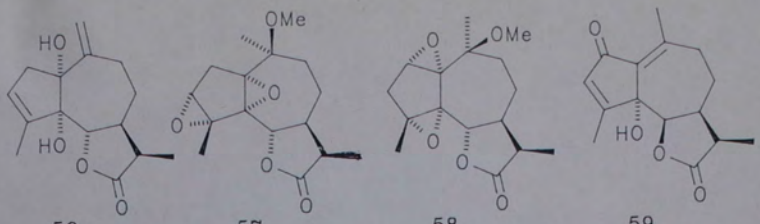
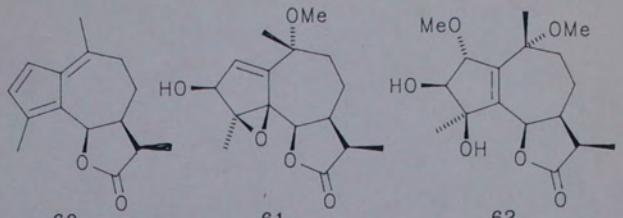


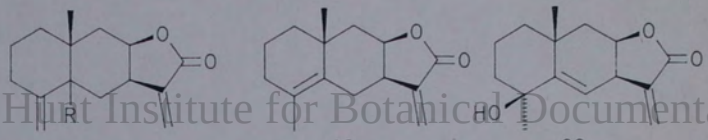
	54	55
X	αOMe,H	O



56 57 58 59



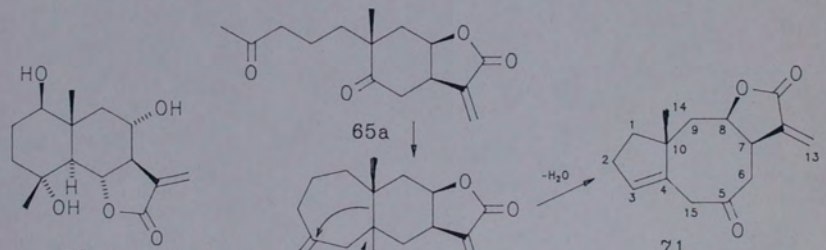
60 61 62



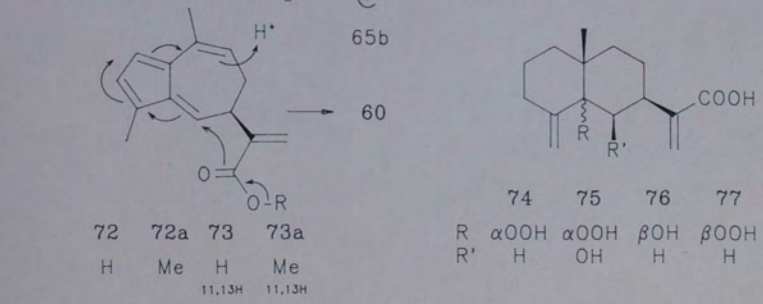
63 64 65 66 67

R αH αOH αOOH βOH βOOH

68 69



70 65a 65b 71



72 72a 73 73a

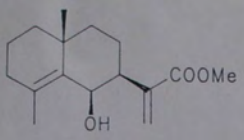
H Me H Me

11,13H 11,13H

74 75 76 77

R αOOH αOOH βOH βOOH

R' H OH H H



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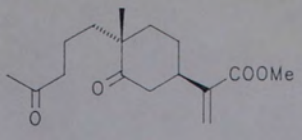

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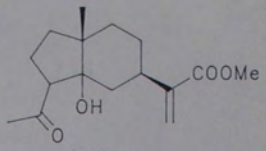

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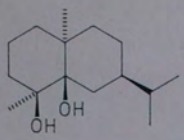

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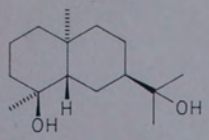

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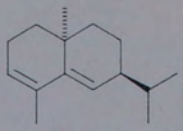

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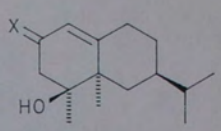
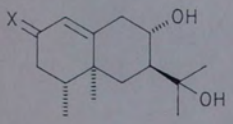
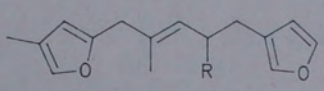


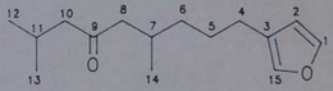
84 85
X αOH,H O



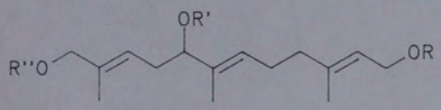
86 87
X αOH,H O



88 89
R H OiVal



90 91 92
Δ^{6E} $\Delta^{6E,10}$



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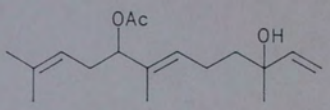

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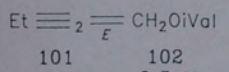

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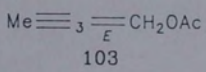

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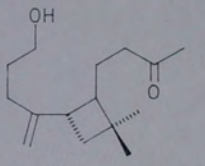

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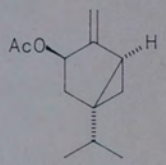

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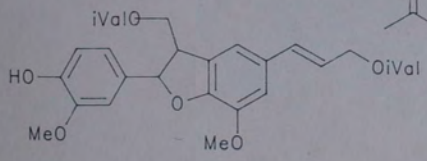

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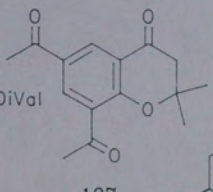

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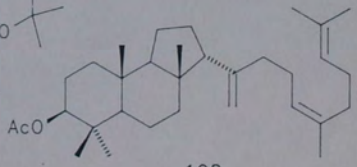

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CASSINI ON COMPOSITAE

COLLECTED FROM THE

DICTIONNAIRE DES SCIENCES NATURELLES

AND ARRANGED WITH

AN INTRODUCTION AND AN INDEX BY

ROBERT M. KING AND HELEN W. DAWSON

ORIOLE EDITIONS NEW YORK

PUBLISHERS

19 WEST 44 STREET NEW YORK NY 10036

(details overleaf)

FUNDACION PARA EL DESARROLLO DE LAS CIENCIAS FISICAS, MATEMATICAS Y NATURALES

EDIF. ICAUCA - MEZZ. 2
PELOTA A PUNCERES
AVDA. URDANETA

TELEFONO 561.35.00
APARTADO No. 1998
CARACAS 1010-A - VENEZUELA

CONVENIO SOBRE LAS PUBLICACIONES CIENTIFICAS

RESULTANTES DE LA EXPEDICION

I. INTRODUCCION

La Fundación para el Desarrollo de las Ciencias Físicas, Matemáticas y Naturales considera que es trascendental dentro de la Expedición al Cerro de La Neblina, lo relativo a los informes escritos sobre los resultados de sus observaciones y trabajos de campo de los investigadores participantes.

Es por ello que se ha designado al Coordinador Ejecutivo y Jefe de la Expedición, Charles Brewer-Carías, como El Editor de las publicaciones, las cuales serán hechas a nombre de la Fundación para el Desarrollo de las Ciencias Físicas, Matemáticas y Naturales, el Instituto Nacional de Parques, el Consejo Nacional de Investigaciones Científicas y Tecnológicas y otras instituciones que manifestaren interés, efectuándose la impresión en Venezuela.

II. PUBLICACIONES

Se han programado tres (3) tipos de publicaciones, en tres etapas distintas, dentro del marco propio de la evolución de las investigaciones:

A. Informe Preliminar / Preliminary Report
B. Resultados de la Investigación / Research Report
C. Catálogo de Separatas de Contribuyentes del Cerro de La Neblina/ Reprint Catalogue

A. INFORME PRELIMINAR / PRELIMINARY REPORT

Se publica inmediatamente al salir el investigador del Campamento. Consiste en una información inicial que debe presentarse antes de abandonar el país, en el caso de científicos visitantes; la cual entre otras cosas muestra el área de exploración, el tema y los resultados en el campo; considerándose básicamente un inventario del trabajo realiza

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do, de manera que los investigadores al llegar al campamento conozcan la evolución de los otros trabajos que se están realizando, contando para ello con un registro confiable, evitando incurrir en duplicación de trabajos y colecciones innecesarias; así mismo se garantiza la calidad de la metodología de trabajo utilizada. Esta publicación podrá ser realizada en forma facsimilar de los informes, para consumo del equipo de investigadores, así como de sus instituciones patrocinantes, a los efectos de permitir un contacto e interrelación más efectivos. Al concluir la expedición se enviará copia del conjunto de informes a cada uno de los participantes inscritos y se encuadernarán las separatas como volúmen de guía y consulta. Para facilitar esta recopilación de información se entregará una carpeta de trabajo a cada investigador, de la cual se podrá sacar de inmediato, con papel carbón, un duplicado para El Editor, sin recargar de trabajo al científico.

El Informe Preliminar / Preliminary Report, contendrá entre otros datos, los siguientes:

* Cronología de ocupación
* Areas geográficas ocupadas en exploración
* Posición en el campamento
* Inventario personal y ocupación, particular y de sus acompañantes.
* Climatología
* Tema(s) desarrollado(s)
* Resultados del trabajo de campo, en forma estimada
* Número de colecciones, su distribución y ubicación.

B. RESULTADOS DE LA INVESTIGACION / RESEARCH REPORT

Al cabo del segundo año de haber sido iniciada la Expedición, cada participante debe someter un papel de trabajo con los resultados de la Exploración e investigación propia, el cual bien puede haber sido publicado anteriormente, pero que definitivamente debe ser realizado para cumplir con la fecha establecida, es decir dos años después de la fecha establecida, es decir dos años después de la echa de inicio de la Expedición. El libro a publicar en esta etapa es la obra principal, ay que contiene los resultados propiamente de la Expedición, y El Editor y responsable principal es el mismo de la anterior.

La publicación se realizará en Español, con resúmenes en inglés de todos los artículos, ilustrándose con fotografías adicionales. El patro

. / .

cinio será el mismo de la obra anterior.

C. CATALOGO DE SEPARATAS DE CONTRIBUYENTES DEL CERRO DE LA NEBLINA / REPRINT CATALOGUE

Dos (2) años después de la publicación de los resultados en Español, se realizará una impresión facsimilar de lo publicado con anterioridad y - posteriormente de la publicación de los RESULTADOS DE LA INVESTIGACION/ RESEARCH REPORT, por los mismos u otros colaboradores; siendo igualmente El Editor el de las dos obras anteriores.

Para cumplir con el propósito de esta publicación, se contará con la colaboración de los investigadores participantes, quienes deberan hacer llegar a la Fundación para el Desarrollo de las Ciencias Físicas, Matemáticas y Naturales, por lo menos un (1) ejemplar de las publicaciones que se hayan realizado hasta esa fecha de sus trabajos en revistas especializadas, así como informar a la Fundación de posibles publicaciones de otros autores producto de las observaciones y colecciones de esta Expedición.

III. NORMAS PARA LOS AUTORES

a. Toda publicación traerá como parte de la Introducción los siguientes créditos para las instituciones organizadoras y la dirección:

" La Expedición al Parque Nacional Cerro de La Neblina ha sido organizada y dirigida por la Fundación para el Desarrollo de las Ciencias Físicas, Matemáticas y Naturales de Venezuela, con el patrocinio del Ministerio de Educación, Consejo Nacional de Investigaciones Científicas y Tecnológicas, Instituto Nacional de Parques, todas ellas instituciones venezolanas, bajo la coordinación del Dr. Charles Brewer-Carías y con la colaboración de la National Science Foundation de los Estados Unidos, la Royal Geographical Society de Inglaterra, y las siguientes instituciones norteamericanas: American Museum of Natural - History, Field Museum of Natural History, National Museum of Natural History, New York Botanical Garden y Smithonian Institution."

b. Todo autor ubicará sobre reproducción de imágen de radar los lugares donde realizó su investigación y la fecha de su exploración.

. / .

c. Toda publicación de autor en revista especializada debera llevar un "Abstract" en español o en inglés, viceversa según la lengua en la cual se hubiere escrito el trabajo. Se deberá incluir la dirección y el número de teléfono para su adecuada localización.

d. Todo participante deberá firmar el presente convenio, y si lo desea podrá anexar comentarios que considera podrán ayudar al Editor en su tarea.

Por la FUNDACION

Francisco Carrillo Batalla
Presidente

Charles Brewer-Carías
El Editor

POR la Institución Investigadora

Investigador:
Cargo:

Lugar y fecha:_____

NOTA: Se envía un juego o set de original y copia por cada investigador. Se agradece devolver el original debidamente firmado y sellado.

c. Toda publicación de autor en revista especializada deberá llevar un "Abstract" en español o en inglés, viceversa según la lengua en la cual se hubiere escrito el trabajo. Se deberá incluir la dirección y el número de teléfono para su adecuada localización.

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Lugar y fecha:

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THE GENERA OF EUPATORIEAE (ASTERACEAE)

R.M. King & H. Robinson

Smithsonian Institution

Starting in 1966 the authors have provided a series of partial revisions of the Eupatorieae, publishing over 200 papers on the group. *The Genera* provides a synthesis of their contributions to our understanding of this species-rich group: one in every 150 species of flowering plants belongs to the Eupatorieae.

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Published as Monographs in Systematic Botany from the Missouri Botanical Garden, volume 22, 580 pages, 8½ by 11 inches, color frontispiece, handbound. October 1987.

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COMPOSITAE NEWSLETTER

Tod F. Stuessy, *Editor*
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Columbus, Ohio 43210, U.S.A.

Robert M. King, *Assoc. Editor*
Department of Botany
Smithsonian Institution
Washington, D.C. 20560, U.S.A.

NUMBER ONE

Considering the profusion of journals and bulletins flooding everyone's laboratory these days, the thought of introducing an additional newsletter is almost too much to bear. Nonetheless, it does seem proper that the numerous systematists working on the large and biologically important family, the Compositae, should have a formal outlet for exchange of information among themselves. It is with this motivation that we offer this first number of the Compositae Newsletter.

We have no particular aspirations for this little bulletin, nor do we feel compelled to publish it at regular intervals. Rather, whenever sufficient information is received to merit costs of duplication and mailing, the Newsletter will be printed and distributed.

We neither encourage nor discourage the submission of any particular type of information; whatever is sent to us will be included with only a minimum amount of editing. The editorial policy, therefore, will be essentially one of non-review. We hope that published items of interest will provoke both positive and/or negative responses from fellow synantherologists, which may result in lively and beneficial discussion not available in most journals.

For purposes of organization, we have chosen seven subheadings for the Newsletter which we believe will accommodate most of the information sent to us. These categories are: (1) Editorials; (2) Points of View; (3) Articles; (4) Book Reviews; (5) Meetings and Other Timely Events; (6) News from Individuals and Institutions; and (7) Requests for Material.

We hope this first number of the Newsletter will reach the majority of workers in the Compositae. Because no mailing list of this sort is ever complete, we would appreciate receiving the names and addresses of people who did not receive the first issue but who would like to receive subsequent ones. Hopefully, at some later date the mailing list can be published along with additional information about each of the workers.

The costs of typing, reproduction, and mailing are for the present being borne by the Departments of Botany of The Ohio State University and the Smithsonian Institution. We wish to acknowledge with thanks the financial and moral support of these institutions and their chairmen.

Meetings and Other Timely Events

It may seem unnecessary to include here a mention of the international symposium on The Biology and Chemistry of the Compositae to be held in Reading, England, 14-18 July. On the chance that some the recipients of the Newsletter are not aware of this meeting, however, a brief description follows.

The University of Southwestern Louisiana

Lafayette, Louisiana 70504-2451

Université des Acadiens

Microscopy Center
P.O. Box 42451
(318) 231-5769

To: Dr. Robert King
Dept. of Botany, Stop #166
Museum of Natural History
Smithsonian Institute
Washington, D.C. 20560

From: Dr. Thomas Pesacreta, Microscopy Center
PO Box 42451, Univ. of Southwestern Louisiana
Lafayette, LA 70504

Dear Dr. King:

Enclosed please find several micrographs which show portions of the stamens of *Cirsium horridulum*. The scanning electron micrograph (SEM) is simply to orient you - I have marked the filament as "F" and the collar as "C".

Figures A and A' show longitudinal views of the collar/filament intersection. The autofluorescence in "A" is most intense in the collar cells that are nearest the filament. Figure B shows the autofluorescence in the portion of the collar nearer to the locules - here the autofluorescence is much less intense. Figure C shows two adjacent collar/filament complexes. It is evident from this data that the autofluorescence is not simply due to the presence of secondary walls, but is most intense in the middle lamella and primary wall regions.

Figure D shows a transverse view of the collar and the staminal appendages (tails). The lack of autofluorescence in the adaxial epidermis of the collar in this species is evident.

I am nearly ready to submit this data along with a SEM/TEM analysis of the collar in *Cirsium*, for publication. Also, we have observed that collar autofluorescence is widespread among the tribes of the Asteraceae, and are preparing an evaluation of the autofluorescent pattens in each species as a taxonomic tool. During the course of this work the question has arisen as to the origin of the term "collar" - I wonder if you could help us out in this regard.

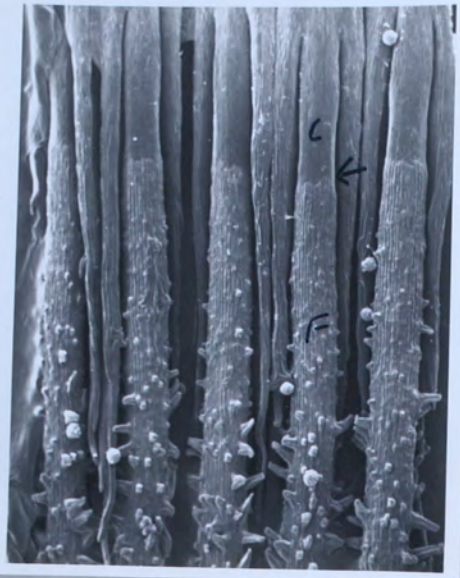
I would also be eager to know about any criticisms or suggestions that you may have regarding this work.

Sincerely,

Tom

Tom Pesacreta

SEM



AUTOFLUORESCENCE OF COLLAR NEAR POINT OF MERGER WITH ANTHER TAILS.

LOCULES

FILAMENT

COLLAR

B