CONSTITUENTS OF *FAGARA MACROPHYLLA* AND *ZANTHOXYLUM RIGIDIFOLIUM* PERICARPS[1]

JOHANNES REISCH, DIETER BERGENTHAL,

Institute for Pharmaceutical Chemistry, University of Münster, Hittorfstrasse 58-62, D-4400 Münster, Federal Republic of Germany

SIMEON K. ADESINA, DOYE D. AKINWUSI,

Drug Research and Production Unit, Faculty of Pharmacy, University of Ife, Ile-Ife, Nigeria

and A.O. OLATUNJI

Department of Botany, Faculty of Science, University of Ife, Ile-Ife, Nigeria

Two issues stimulated our interest in the chemistry of the pericarps of these plants. The first was the taxonomic position of *Zanthoxylum rigidifolium* (Herzog) Waterm. [syn. *Zanthoxylum tessmannii* (Engl.)

TABLE 1. Volatile Constituents of *Fagara macrophylla* Pericarp

Component	Mass *m/z*	100 (%) *m/z*	Concentration (%)	Source of Identification
3,3-dimethylhexane	114	43	tr[a]	ms[b]
4-ethylcyclohexanone	126	55	tr	ms
α-pinene	136	93	3.60	ms, rt[c]
camphene	136	93	tr	ms
3-carene	136	93	tr	ms, rt
β-pinene	136	93	tr	ms, rt
limonene	136	68	1.00	ms, rt
1,3,5-trimethylbenzene	120	105	tr	ms
2,3,6-trimethyl-1,5-heptadiene	138	69	tr	ms
2,7-dimethyl-2,6-ocatdiene	138	69	tr	ms
borneol	154	59	0.40	ms, rt
unknown	170	59	tr	un-identified
linalool	154	71	2.92	ms, rt
undecane	156	57	nd[d]	ms
codecane	170	57	nd	ms
bornyl acetate	196	95	0.23	ms, rt
guaia-1(5),7(11)-diene	204	105	0.29	ms
δ-guaiene	204	41	7.12	ms
franesol isomer	222	69	0.59	ms, rt
farnesol isomer	222	69	0.61	ms, rt
camphor	152	152	6.22	ms
syringaldehyde	182	182	6.49	ms, rt
methyl hexadec-11-enoate	268	55	tr	ms
11-hexadec-enoic acid	254	55	tr	ms
2-ketotridecan-1-yl acetate	256	43	2.20	ms
hexadecanoic acid	256	43	tr	ms, rt
methyl eugenol	178	178	4.68	ms, rt
3-(2-pentenyl)-1,2,4-cyclopentanetrione	180	69	45.17	ms
9,12-octadecadienoic acid	180	55	0.46	ms, rt
9-octadecenoic acid	282	55	0.41	ms, rt
scopoletin	192	192	0.90	ms, ir, uv, rt

[a]tr = traces (<0.1).
[b]ms = mass spectrum.
[c]rt = retention time.
[d]nd = not determined.

[1]Paper 106 in the series "Natural Product Chemistry." For part 105, see J. Reisch *et al* (16).

Ayafor, Rutaceae] and *Fagara macrophylla* Engl. (syn. *Zanthoxylum gilletti*, Rutaceae). The view that *Z. rigidifolium* may be synonymous (1) with *F. macrophylla* was corrected by two earlier reports (2,3). A chemical study (4) of *Z. rigidifolium* led to the identification of lupeol, nitidine, fagaridine, chelerythrine, and fagaramide, and to the suggestion that *Z. rigidifolium* may be synonymous with *F. macrophylla* which contained (5,6,7) nitidine, chelerythrine, dihydrochelerythrine, fagaramide, and skimmianine. Second was the observation that insects are usually attracted in large numbers to the flowers and fruits of both species.

TABLE 2. Volatile Constituents of *Zanthoxylum rigidifolium* Pericarp

Component	Mass *m/z*	100(%) *m/z*	Concentration (%)	Source of Identification
methane	140	97	nd[a]	ms[b]
1,3,5-trimethylbenzene	120	105	nd	ms
decane	142	43	nd	ms
2,7-dimethyl-2,6-octadiene	138	69	tr[c]	ms
2-phenylbutane	134	105	nd	ms
undecene	154	69	nd	ms
undecane	156	43	nd	ms
4-isobutyltoluene	148	105	nd	ms
methylundecane	170	57	nd	ms
azulene	128	128	1.54	ms
dodecane	170	57	nd	ms
geranial	152	41	tr	ms
tridecene	182	43	nd	ms
tridecane	184	57	nd	ms
tetradecene	196	43	nd	ms
tetradecane	198	57	nd	ms
trans-β-farnesene	204	69	1.70	ms, rt[d]
β-bisabolane	210	55	2.70	ms
pentadecane	212	57	3.00	ms
α-farnesene	204	41	tr	ms
nerolidol	222	43	9.03	ms
2,3-dihydrofarnesal	222	69		ms
heptadecene	238	41	8.92	ms
2,3-dihydrofarnesol	224	69		ms
heptadecane	240	43	3.06	ms
2,3-dihydrofarnesyl acetate	266	69	6.70	ms
farnesyl acetate	264	69	9.34	ms
nonadecane	268	57		ms
methyl hexadecanoate	270	74	tr	ms
hexadecenoic acid	254	41	tr	ms
2-keto-tridecan-1-yl acetate	256	43	15.66	ms
hexadecanoic acid	256	43		ms
eicosane	282	43	nd	ms
heptadecanoic acid	270	43	tr	ms
methyl linolenate	294	55	3.03	ms
9,12-octadecadienoic acid	280	55	1.20	ms, rt
9-octadecenoic acid	282	55	1.57	ms
octadecanoic acid	284	43	tr	ms, rt
docosane	310	57	nd	ms
tricosane	324	57	nd	ms
nonacosane	408	57	nd	ms
hentriacontane	436	57	nd	ms, rt
asarinin	354	149	7.14	ms
sitosterol	414	43		ms, rt

[a]nd=not determined.
[b]ms=mass spectrum.
[c]tr=traces (<0.1).
[d]rt=retention time.

Plant primary and secondary products are deeply implicated in insect behavior such as feeding, reproduction, and defense. It was thought that a chemical study of the pericarps may help to clarify this taxonomic problem as well as determine the nature of insect attractants in these plants.

Analysis of the pericarps by capillary gc/ms and cc monitored by tlc led to the identification of the compounds shown in Tables 1 and 2. The patterns of the uv-absorbing chemicals in both pericarps differ very much as observed by 1-D and 2-D tlc and pc. While long-chain alkanes and alkenes, farnesyl derivatives, and sterols represent the major constituents of *Z. rigidifolium* pericarps, terpene hydrocarbons, aldehydes, ketones, and scopoletin were found in *F. macrophylla* pericarps. Oxidized and reduced forms of compounds characterize the constituents of both pericarps. These chemical variations and the morphological differences previously described (2,3) confirm that these plants represent two distinct species.

The identification of 2-ketotridecan-1-yl acetate, eugenol derivatives, hexadecenoic acid, alkanes and alkenes, terpenes, and ketones in the pericarps explains why insects are usually seen attracted to these organs. Some of these components have been implicated (8-15) as insect attractants.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Analysis and identification were performed on a Varian CH 7A mass spectrometer coupled with a GC Varian Model 3700 and completed with a data bank. The conditions of analysis were as described earlier (16): gc parameters: He at pre-pressure of 0.6 bar, temperature programmed 80° to 260° at 6°/min, injector temperature at 300°; quartz capillary column (50 m, 0.7 mm i.d.; Macherey and Nagel) coated with OV 101; split valve 1:10; injection volume 4 μl. The final temperature was maintained for 40 min. The ir spectra were taken as KBr pellets and the uv spectra in EtOH.

COLLECTION AND IDENTIFICATION OF PLANT MATERIALS.—The plant materials were collected and identified by one of us (OAO), and voucher specimens of *Z. rigidifolium* (Olat. 573) and *F. macrophylla* (Olat. 595) were deposited at the Dept. of Botany, University of Ife, Ile-Ife, Nigeria.

PREPARATION OF SAMPLES FOR ANALYSES.—Whole fruits were air dried in the dark at room temperature which permitted the separation of the pericarp from the seed. The dried and ground *Z. rigidifolium* pericarp (57 g) and *F. macrophylla* pericarp (51 g) were separately covered with AR CH_2Cl_2 and shaken for 1 week. These extracts were analyzed directly by gc, tlc, and gc/ ms. MeOH extracts of the ground pericarps were prepared for analysis by cc and tlc.

CHARACTERIZATION OF COMPONENTS.—Gc retention times (rt) were noted for volatile constituents. Peak enlargements, resulting from co-gc with authentic compounds, and data from gc/ms and computer assisted mass spectral analyses led to conclusive identifications of many components.

The spectra of compounds were compared with those of authentic samples, with published data, or with the spectra of known isolated chemicals. Scopoletin (29 mg, mp 205°) was isolated from *F. macrophylla* pericarp extract on column-chromatography and identified by its mp, ir, ms, uv, and chromatographic behavior.

ACKNOWLEDGMENTS

This research was supported by the Deutsche Forschungsgemeinschaft and a grant from the Heinrich-Hertz-Stiftung to one of us (SKA).

LITERATURE CITED

1. A.G. Voorhoeve, "Liberian High Forest Trees," Centre for Agric. Publications and Documentations, Wageningen, Netherlands, 1965, p. 335.
2. O.A. Olatunji, *Bull. Sci. Assoc.* (Nigeria), **2**, 62 (1976).
3. O.A. Olatunji, *Nig. J. Sci.*, **80**, in press.
4. I. Addae-Mensah and E.A. Sofowora, *Planta Med.*, **35**, 94 (1979).
5. F.G. Torto, P. Sefcovic, B.A. Dadson, and I. Addae-Mensah, *Ghana J. Sci.*, **9**, 3 (1969).
6. F.G. Torto and I. Addae-Mensah, *Phytochemistry*, **9**, 911 (1970).
7. F. Fish and P.G. Waterman, *J. Pharm. Pharmacol.*, **23**, 67 (1971).
8. C.G. Bulter, D.H. Calam, and R.K. Callow, *Nature*, **213**, 423 (1967).
9. C.G. Butler and D.H. Calam, *J. Insect. Physiol.*, **15**, 237 (1969).
10. M. Géllert, Zs. Rózsa, Z. Kovacs, K. Szendrei, R.A. Hussain, G. Reisch, and J. Reisch, *Herba Hung.*, **24**, 53 (1985).
11. I.H. Williams, J.A. Pickett, and A.P. Martin, *J. Chem. Ecol.*, **7**, 225 (1981).
12. J.G. Kostlc, J.E. Girard, and L.B. Hendry, *J. Chem. Ecol.*, **6**, (1980).
13. D.R. Nelson, J.W. Dillwith, and G.J. Blomquist, *Insect Biochemistry*, **11**, 187 (1981).
14. H.M. Flint, J.R. Merkle, and M. Sledge, *Environ Entomol.*, **10**, 301 (1981).
15. J.A. Picket, I.H. Williams, A.P. Martin, and M.V. Smith, *J. Chem. Ecol.*, **6**, 425 (1980).
16. J. Reisch, S.K. Adesina, D. Bergenthal, and R.A. Hussain, *Sci. Pharm. (Wien)*, **53**, 153 (1985).

Received 3 June 1986