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SHORT COMMUNICATION

GAS CHROMATOGRAPHIC ANALYSES OF THE FURANOSESQUITERPENES OF *LINDERA STRYCHNIFOLIA* IN PLANT MATERIALS OF DIFFERENT GEOGRAPHIC ORIGIN[1]

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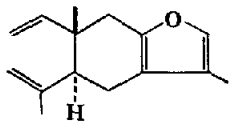
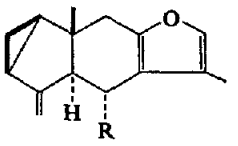
Abstract—Four samples of *Lindera strychnifolia*, each of different geographical origin, varied considerably in their furanosesquiterpene content.

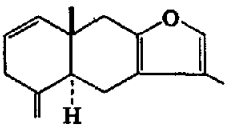
WE PREVIOUSLY[2] reported the isolation of isofuranogermacrene (I) from the ether extract prepared by Suzuki[3] from a Chinese drug "T'ien t'ai wu yao" (dried roots of *Lindera strychnifolia* Vill—Lauraceae) purchased at a Taipei market in Formosa (Material A).* Later we also isolated lindenene (II),[4] in addition to isofuranogermacrene (I)[2] and lindestrene (III),[5] from an ether extract of this plant collected in Miye Prefecture, Japan (Material C). At that time[4] we learned that, as lindenene (II) formed an intimate mixture with lindestrene (III), it was impossible to distinguish between these two components by GLC run under the conditions described for separation of isofuranogermacrene and "lindestrene".[2] This required re-examination of the liquid furanosesquiterpene region of "Material A" to confirm whether the "lindestrene" contains lindenene or not.



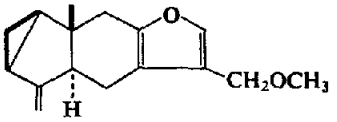
Isofuranogermacrene (I)



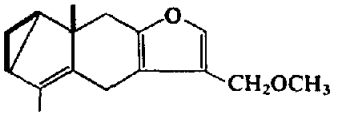
Lindenene (II, R = H)
Lindenenol (VII, R = OH)



Lindestrene (III)



Linderoxide (IV)



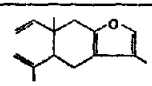
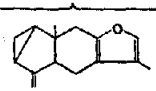
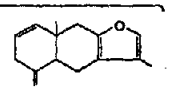
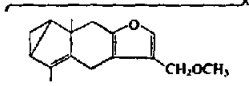
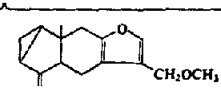
Isolinderoxide (V)

CHART 1.

* This material was assumed to be of Chinese origin gathered from Chekiang Province.

[1] Part XIX in the series "Components of the Root of *Lindera strychnifolia*"; for Part XVIII see H. TADA, H. MINATO and K. TAKEDA, *J. Chem. Soc.* (C), in press.
[2] H. ISHII, T. TOZYO, M. NAKAMURA and K. TAKEDA, *Tetrahedron* **24**, 625 (1968).
[3] H. SUZUKI, *J. Pharm. Soc. Japan* **50**, 714 (1930).
[4] K. TAKEDA, H. ISHII, T. TOZYO and H. MINATO, *J. Chem. Soc.* (C) 1920 (1969).
[5] K. TAKEDA, H. MINATO, M. ISHIKAWA and M. MIYAWAKI, *Tetrahedron* **20**, 2655 (1964).

TABLE 1. LIQUID FURANOSESQUITERPENES IN MATERIAL A

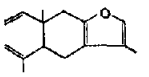
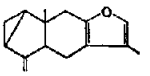
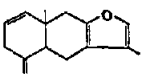
B.p. (°C/2 mm)	Wt (g)	Fraction 2 (%)	GLC analysis  (%)	 (%)	 (%)	Fraction 3 (%)	GLC analysis  (%)	 (%)
–116	14·7	12	75 (9)*	6 (1)	16 (2)	—	—	—
116–125	5·0	30	30 (9)	14 (5)	40 (12)	9	55 (5)	45 (4)
125–130	3·8	32	12 (4)	19 (6)	64 (21)	16	50 (8)	50 (8)
130–135	4·8	20	—	17 (3)	65 (13)	34	37 (13)	63 (21)
135–140	1·3	10	—	13 (1)	67 (7)	62	30 (19)	70 (43)
140–145	5·4	8	—	15 (1)	68 (6)	83	24 (20)	76 (63)
Total %	100		5·5	2·4	7·8		7·2	15·6

* Figures in parentheses show the percentage of the compound in each distillation fraction.

A part of each distillation fraction[2] was further divided by chromatography on alumina into four fractions: (1) a mixture of hydrocarbons, (2) a mixture of the least polar furanosesquiterpenes, (3) a mixture of methoxyl-containing furanosesquiterpenes [linderoxide (IV)[2] and isolinderoxide (V)],[6] and (4) a crystalline mixture of further oxygenated sesquiterpenes. Fraction 2 was submitted to analytical GLC under the conditions used for detection of lindenene,[4] and we found that the "lindestrene", which had been regarded as a single substance in an earlier experiment,[2] was about one-quarter lindenene. The analytical results on fractions 2 and 3 are summarized in Table 1.

About 30 years ago, one of us (K. T.) prepared an ether extract from another lot of the Chinese drug (Material B) purchased from a Shanghai market, and fractionated it by distillation.[7] One of the fractions (b.p. 100–140°/4 mm) was re-distilled, and the resulting eight distillation fractions were sealed in ampoules and remained untouched. This affording a good opportunity, we have also analysed these eight samples in the same manner as described for "Material A". The results are shown in Table 2.

TABLE 2. LIQUID FURANOSESQUITERPENES IN MATERIAL B

B.p. (°C/2 mm)	Wt (g)	Fraction 2 (%)	GLC analysis  (%)	 (%)	 (%)	Benzofuran compound (%)
–115	4·2	12	75 (9)*	6 (1)	12 (2)	—
115–120	2·5	29	50 (15)	11 (3)	24 (7)	7 (2)
120–125	20·0	39	33 (13)	16 (6)	33 (13)	11 (4)
125–130	3·5	36	7 (3)	23 (8)	47 (17)	18 (6)
130–135	1·5	27	6 (2)	21 (6)	54 (15)	18 (5)
135–140	8·9	21	—	26 (5)	53 (11)	16 (3)
140–150	31·5	10	—	23 (2)	52 (5)	23 (2)
150–160	6·5	3	—	11 (0)	30 (1)	35 (1)
Total %	100		4·4	3·5	8·8	2·7

* Figures in parentheses show the percentage of the compound in each distillation fraction.

"Material B" did not possess linderoxide (IV) and isolinderoxide (V), but contained an unidentified compound (VI), a colorless oil, $C_{15}H_{16}O$, which was assumed to be a sesquiterpenoid having a benzofuran moiety in the molecule from its elemental analysis as well as from its u.v. and NMR spectra. Considering this partial structure, it might be an artifact produced on repeated distillation by dehydrogenation of another furanosesquiterpene.

Recently we have received another sample of this plant, collected in Formosa (Material D), and prepared its least polar furanosesquiterpene fraction according to the procedure for "Material C".[4] GLC inspection of the fraction showed it to contain isofuranogermacrene (2·5%), lindenene (48·5%) and lindestrene (49%).

Since we now have analytical results on the furanosesquiterpenes in four samples, "Materials A, B, C* and D", we can compare them by representing the quantity of lindestrene (II), a common major constituent, as 100 (see Table 3).

* In this material, isofuranogermacrene, lindenene and lindestrene occurred in a ratio of 6:33:61.[4]

[6] K. TAKEDA, H. MINATO, I. HORIBE and M. MIYAWAKI, *J. Chem. Soc.* (c) 631 (1967).
[7] H. KONDO and K. TAKEDA, *J. Pharm. Soc. Japan* 59, 504 (1939).

TABLE 3. COMPARISON OF THE RATIO OF LIQUID FURANOSESQUITERPENES IN FOUR SPECIMENS OF *Lindera strychnifolia* ROOT

Compound	Material			
	A	B	C	D
Isofuranogermacrene (I)	70	50	10	5
Lindenene (II)	30	40	55	100
Lindestrene (III)	100	100	100	100
Benzofuran (VI)	—	30	—	—
Isolinderoxide (V)	95	—	—	—
Linderoxide (IV)	200	—	—	—

Of the four materials examined, "Material A" alone* yielded the methoxyl-containing compounds, linderoxide and isolinderoxide, in quantity. Since Suzuki[3] reported that this material contained very little lindenenol (VII),[4] which is usually one of the main crystalline constituents in this plant, it may be reasonable to consider that "Material A" produced linderoxide and isolinderoxide, through a different oxidation route, from an intermediate common to lindenenol in the biogenetic pathway.

EXPERIMENTAL

Chromatography on Alumina of the Distillation Fractions from "Materials A and B"

About 100 mg of each distillation fraction (see Tables 1 and 2) was weighed accurately and chromatographed on alumina (activity II, 10 g). The first elution with *n*-pentane gave a mixture of non-polar hydrocarbons (Fraction 1), which gave a negative Ehrlich test. Successive elution with *n*-pentane yielded a mixture of the least polar furanosesquiterpenes (Fraction 2). Elution with *n*-pentane–ether (95:5) provided a mixture of linderoxide (IV) and isolinderoxide (V) (Fraction 3). The final elution with ether afforded a mixture of the more polar components (Fraction 4).

From the weight of each Fraction 2 and 3, the percentage of these fractions in each distillation fraction was calculated (see tables).

Analytical GLC

Analytical GLC was run on an Aerograph Autoprep A-700 instrument using 10 ft × ⅜ in. o.d. columns. Retention times of isofuranogermacrene (I), lindenene (II), lindestrene (III) and benzofuran compound (VI) were 13, 31·5, 35 and 40 min, respectively (5% DEGS; 140°; He 100 ml/min). Retention times of isolinderoxide (V) and linderoxide (IV) were 5·5 and 7·5 min, respectively (1% SE-30; 150°; He 200 ml/min).

The percentage of each compound in Fraction 2 or Fraction 3 was calculated on the basis of peak area.

Isolation of the Liquid Furanosesquiterpene Fraction from "Material D"

Dried and sliced roots of *Lindera strychnifolia* Vill. (500 g), collected in Formosa in 1967, were extracted with ether (3 × 3 l.) at room temperature for 3 days. The combined extracts were evaporated to leave a brown viscous oil (20·5 g), which was dissolved in a mixture of ether (50 ml) and light petroleum (30 ml). The solution was left in a refrigerator to yield 2·48 g of ppt. The mother liquor was evaporated to dryness, dissolved in light petroleum, and chromatographed on alumina (activity IV, 200 g), giving a least polar fraction (5·62 g). This fraction was rechromatographed on alumina (activity II, 200 g) and eluted with light petroleum to give two portions, a mixture of non-polar hydrocarbons (1·64 g) and a mixture of the least polar furanosesquiterpenes (3·52 g). The latter showed three peaks on GLC due to isofuranogermacrene (2·5%), lindenene (48·5%) and lindestrene (49%).

Acknowledgements—We thank Prof. Y. H. Kuo of National Taiwan University and Mr. M. Kawaguchi (Owase City, Miye Prefecture) for collection of the plant materials.

* We have found that another specimen of "T'ien t'ai wu yao" (so-called Chinese origin) purchased from a Japanese market contained a small amount of the methoxyl-containing compounds.