using the standard drop-diffusate technique [2] in which a conidial suspension of *Helminthosporium carbonum* Ullstrup acted as the inducing agent, and in MeOH extracts of etiolated epicotyls treated with $HgCl_2$ solution (5×10^{-4} M). Variabilin was previously known as a constituent of *Dalbergia variabilis* [12] and has been reported to occur in infected red clover leaves [10].

The exact role and relative importance of the various phytoalexins in restricting fungal invasion of the lentil is not known and more detailed quantitative studies are required; such studies may be complicated by the presence of other, as yet unidentified, antifungal compounds in extracts of infected tissue. It is interesting that in the cotyledons of *L. culinaris* wyerone epoxide occurs in greater concentrations than wyerone, a reversal of the situation in *V. faba* [3, 6]. Provisional investigations indicate, however, that the concentration of wyerone epoxide present in infected *Lens* cotyledons is significantly lower than that reported for *V. faba* [3] and that wyerone occurs only in comparatively trace amounts in the lentil.

When the cotyledons of *Pisum sativum* L. cv Dorina and *Lathyrus sativus* L. cv Canberra City were challenged with spore suspensions of *B. cinerea* and extracts of infected tissue subjected to TLC as described above furanoacetylenic phytoalexins were not detected. Instead pisatin accumulated to relatively high concentrations (1015 and 454 μg/g fr. wt respectively).

The multiple phytoalexin response of *Lens* is clearly different to any that has previously been described but it is similar to that of *V. faba* which is known to produce small amounts of the isoflavonoid medicarpin (**5**) [13] in addition to the furanoacetylenic phytoalexins. The relationship of *Lens* to *Vicia* and/or *Lathyrus* has long been a subject of controversy. No evidence has yet been found for the occurrence of pisatin in *Vicia* or *Lens* and although certain *Lathyrus* spp. produce variabilin and/or medicarpin as a minor component of their phytoalexin response [7] the apparently rare ability to synthesise the furanoacetylenes wyerone and wyerone epoxide links *Lens* and *Vicia* very closely and at the same time distinguishes them from *Pisum* and *Lathyrus*. Thus it would appear that there is a distinct dichotomy as regards phytoalexin induction within the tribe Vicieae.

Acknowledgements—The author wishes to thank R. W. Butters for mass spectrometry, Dr J. W. Mansfield for a sample of wyerone, and Prof. J. B. Harbone for encouragement and advice. Financial assistance from the S.R.C. and I.C.I. Plant Protection Ltd., is gratefully acknowledged.

REFERENCES

1. Ingham, J. L. and Harborne, J. B. (1976) *Nature* **260**, 241.
2. Ingham, J. L. (1976) Ph. D. Thesis, University of Reading.
3. Hargreaves, J. A., Mansfield, J. W., Coxon, D. T. and Price, K. R. (1976) *Phytochemistry* **15**, 1119.
4. Kupicha, F. K. (1974) Ph. D. Thesis, University of Edinburgh.
5. Robeson, D. J. and Harborne, J. B. (1977) *Z. Naturforsch.* **32c**, 289.
6. Hargreaves, J. A., Mansfield, J. W. and Coxon, D. T. (1976) *Phytochemistry* **15**, 651.
7. Robeson, D. J. Unpublished.
8. Merck, E. (1974) *Dyeing Reagent for Thin Layer and Paper Chromatography*. Merck, Darmstadt, Germany.
9. Fawcett, C. H., Spencer, D. M., Wain, R. L., Fallis, A. G., Jones, E. R. H., Le Quan, M., Page, C. G., Thaller, V., Shubrook, D C. and Whitman, P. M. (1968) *J. Chem. Soc.* (*C*) 2455.
10. Bilton, J. N., Debnam, J. R. and Smith, I. M. (1976) *Phytochemistry* **15**, 1411.
11. Ingham, J. L. (1976) *Phytochemistry* **15**, 1489.
12. Ollis, W. D. (1968) *Recent. Advances in Phytochemistry* (Mabry, T. J., Alston, R. E. and Runeckles, C. V. eds) Vol. I, p. 329. North Holland, Amsterdam.
13. Hargreaves, J. A., Mansfield, J. W. and Coxon, D. T. (1976) *Nature* **262**, 318.

Phytochemistry, 1978, Vol 17, pp. 808–809 Pergamon Press Printed in England

ESSENTIAL OIL FROM CHINESE DRUG 'CAODOUKOU', THE SEEDS OF *ALPINIA KATSUMADAI*

YASUHISA SAIKI*, YOHKO ISHIKAWA†, MITSUO UCHIDA† and SEIGO FUKUSHIMA†

*Faculty of Pharmaceutical Sciences, Kôbe-Gakuin University, Tarumi-ku, Kôbe 673 Japan;
†Shizuoka College of Pharmacy, Shizuoka-shi 422 Japan

(*Received* 3 *November* 1977)

Key Word Index—*Alpinia katsumadai*; Zingiberaceae; caodoukou; essential oil; monoterpenoids; sesquiterpenoids.

Chinese drug 'caodoukou' has been used as a remedial agent for malaria, for cancer-like symptoms of the stomach and throat and for nausea associated with pregnancy (1). This drug was regarded as originating from the seeds of *Alpinia katsumadai* Hayata a zingiberaceous plant native in Hainan Island of southern China (1).

Steam distillation of the drug affords an essential oil in about 1.5% yield. GLC (SE 30) of the oil showed the presence of 22 components. Three main components were isolated and identified as 1,8-cineole, α-humulene and *trans, trans*-farnesol by comparison with their spectral data.

By GC–MS of 8 other constituents were identified as

linalol, camphor, terpinen-4-ol, carvotanacetone, bornyl acetate, geranyl acetate, methyl cinnamate and nerolidol. Six other components were found and presumed to be either sesquiterpene alcohols or monoterpenoid compounds on the basis of the MS but could not be identified absolutely [2, 3].

Caodoukou was previously believed to come from the seeds of *Amomum globosum* Lour [4]. According to Lawrence *et al.* [5], the essential oil of the title plant contains mainly camphor and bornyl acetate and thus their results differ from our data.

EXPERIMENTAL

GLC was on 10% SE-30 at 150° with N_2 50 ml/min. 1,8-Cineole, α-humulene and *trans*, *trans*-farnesol were isolated and identified from their IR, NMR and MS with authentic samples. GC–MS was carried out as for GLC but with He of 40 ml/min as carrier gas and column temps of 150 and 170°. Ionization voltage was 80 eV.

Acknowledgement—We thank Mr Seiji Katayama of Shizuoka College of Pharmacy for measurement of NMR spectra.

REFERENCES

1. Anon. (1961) *Chun-yao-zhi (Peking)* II, 361.
2. Stenhagen, E., Abrahamsson, S. and McLafferty, F. W. (1974) *Registry of Mass Spectral Data.* Wiley, New York.
3. Cornu, A. and Massot, R. (1966) *Compilation of Mass Spectral Data* pp. B 42, 43, B75, B79. Heyden & Son, Paris.
4. Kimura, K. and Konoshima, M. (1956) *Yakuyô-shokubutsugaku-kakuron (Hirokawa)* 61.
5. Lawrence, B. M., Hogg, J. W., Terhune, S. J. and Pichitakul, N. (1972) *Phytochemistry* **11**, 1534.

Phytochemistry, 1978, Vol 17, pp 809–810 Pergamon Press Printed in England

GUAIEN-(5)-OL-(11), EIN NEUER GUAIAN-ALKOHOL AUS GURJUN-BALSAM

GERHARD RÜCKER* und FRIEDRICH WILHELM HEFENDEHL†

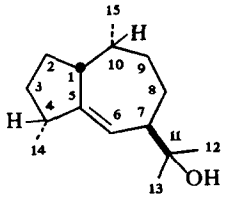
*Institut für Pharmazeutische Chemie der Westf. Wilhelms-Universität, Münster, Hittorfstraße 58, D-44 Münster; †Institut für Pharmazeutische Biologie der Universität Freiburg, Schänzlestraße 9/11, D-78 Freiburg, W. Germany

(*Received* 24 *October* 1977)

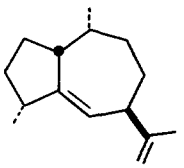
Key Word Index—*Dipterocarpus*; Dipterocarpaceae; gurjun-Balsam; guaien-(5)-ol-(11); new guaiane alcohol

Für Gurjun-Balsam aus verschiedenen *Dipterocarpus*-Arten des asiatischen Raumes (Dipterocarpaceae) [1, 2] ist das Vorkommen von Sesquiterpen-Kohlenwasserstoffen charakteristisch [1–5]. Hinweise auf oxigenierte Sesquiterpene sind spärlich und unklar.

Auf Sumatra werden zwei Typen Gurjun-Balsam gehandelt, von denen eine durch einen hohen Gehalt an α-Copaen, die andere an α-Gurjunen charakterisiert ist [3]. Im letzteren Balsam befindet sich neben einer Reihe von Sesquiterpen-Kohlenwasserstoffen ein Sesquiterpen-Alkohol $C_{15}H_{26}O$ (**1**), der aus dem Rohbalsam durch fraktionierte Wasserdampfdestillation, sc und gc isoliert wurde. ^{1}H-NMR, ^{13}C-NMR und IR zeigen eine trisubstituierte Doppelbindung und damit eine bicyclische Grundstruktur. Aus dem 100%-Peak des MS bei *m/e* = 59 [6] sowie dem Signal für zwei Methyl-Gruppen im ^{1}H-NMR bei δ = 1.14 und 1.16 ppm ergibt sich, daß eine Hydroxy-isopropyl-Gruppe vorliegt. Dies wird durch Dehydratisierung bestätigt: in den Dehydratisierungsprodukten **2** and **3** ist eine Isopropenyl-bzw. eine Isopropyliden-Gruppe nachweisbar (IR, ^{1}H-NMR). **1** läßt sich nicht durch CrO_3/H_2SO_4 oxidieren. Im ^{1}H-NMR (Tabelle 1) koppelt das Signal des olefinischen Protons bei δ = 5.37 mit einem Multiplett (1H) bei δ = 3.00 ppm. Mit dem Shift-Reagenz Eu(FOD)$_3$ nimmt die Verschie-



1



2

Tabelle 1. ^{1}H-NMR-Daten von **1** ($CDCl_3$) und **3** (CD_2Cl_2) (δ-Werte in ppm, 90 MHz, TMS als innerer Standard; *s* = Singulett, *d* = Dublett, *t* = Triplett, *m* = Multiplett)

	1	Δδ*	3
4-H			*t* 2.90
6-*H*	*m* 5.37	1.52	*s* 6.13
7-*H*	*m* 3.00	1.27	
8-*H*			*m* 2.29
12, 13-*H*	*s* 1.14		*s* 1.69
	s 1.16	2.07	*s* 1.73
14-*H*	*d* 1.02	0.34	*d* 1.08
	$J_{4,14}$ = 6.5 *Hz*		$J_{4,14}$ = 7.04 *Hz*
15-*H*	*d* 0.77	0.25	*d* 0.80
	$J_{10,15}$ = 6.5 *Hz*		$J_{10,45}$ = 7.0 *Hz*

* Mit 0.8 Mol Eu(FOD)$_3$-d_{27} (Merck).

* IUPAC-Nomenklatur: 3,8-Dimethyl-5-(α-hydroxy-isopropyl)-1,2,3,5,6,7,8,8a-octahydroazulen.