Phytochemistry, 1980, Vol. 19, pp. 681–682. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0401-0681 $02.00/0

DEHYDRODIEUGENOLS FROM *OCOTEA CYMBARUM**

AURA M. P. DE DIAZ, HUGO E. GOTTLIEB† and OTTO R. GOTTLIEB‡

Instituto Nacional de Pesquisas da Amazônia, Conselho Nacional de Desenvolvimento Cientifico e Tecnológico, Manaus, Amazonas, Brazil

(*Received* 18 *June* 1979)

Key Word Index—*Ocotea cymbarum*; Lauraceae; essential oil; dehydrodieugenols.

Abstract—The trunk wood of *Ocotea cymbarum* from the Amazon basin contains α-phellandrene, α-pinene, eugenol, dehydrodieugenol and its monomethyl ether, as well as the previously unknown dehydrodieugenol-B (4,5′-diallyl-2′-hydroxy-2,3′-dimethoxydiphenyl ether).

INTRODUCTION

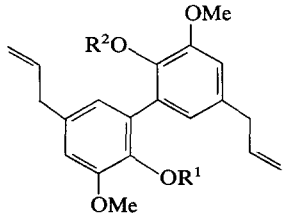
During World War II, subsequent to the interruption of trade with Japan, 'oil of sassafras' from Santa Catarina State, Brazil, became a major source of safrol. Since 'oil of sassafras' refers to the essential oil of *Sassafras albidum* (Nutt.) Nees (Lauraceae), U.S. Customs officials suggested adoption of a name referring to botanical source and the Brazilian product was exported for many years under the designation 'essential oil of *Ocotea cymbarum*' [2]. The correct binomial for the above species is actually *O. pretiosa* (Nees) Mez (Lauraceae), but at that time this was rejected by botanists, due to the fact that Mez had stressed the strong cinnamon odour of its wood as a predominant character [3]. Sassafras wood from Santa Catarina, however, smells strongly of safrol. The phenomenon was later shown to be due to physiological variation and chemical aspects were elucidated [4–6].

We have now been able to collect a sample of authentic *Ocotea cymbarum* (H.B.K.) Nees and here report the analysis of its chemical constituents.

RESULTS

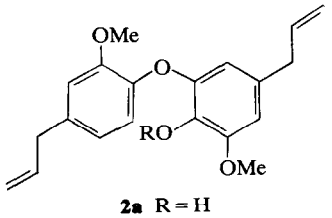
O. cymbarum occurs in the Amazon basin. Vapour entrainment of its trunk wood gave an essential oil consisting chiefly of α-phellandrene, accompanied by its decomposition product *p*-cymene, as well as by α-pinene and by trace amounts of β-pinene and eugenol. Safrol was not detected.

Solvent extraction of the wood led to three compounds, dehydrodieugenol (**1a**), previously isolated from *Litsea turfosa*, an Indian Lauracea [7], its monomethyl ether (**1b**) and a novel oxidative dimer of eugenol designated dehydrodieugenol-B (**2a**). Dehydrodieugenol (**1a**) was identified by direct comparison with a synthetic sample [8, 9].



1a $R^1 = R^2 = H$
1b $R^1 = H$, $R^2 = Me$
1c $R^1 = Ac$, $R^2 = Me$
1d $R^1 = R^2 = Me$

The novel *O*-methyldehydrodieugenol (**1b**) gave an acetate (**1c**) which helped structural characterization by spectral means. As expected, the synthetic mono-*O*-methyl derivative of **1a** was identical with the natural compound (**1b**). The MS of natural **1b** contained a relatively feeble peak at *m/e* 354. The dimethyl ether of **1a**, di-*O*-methyldehydrodieugenol (**1d**), may thus also occur in nature.



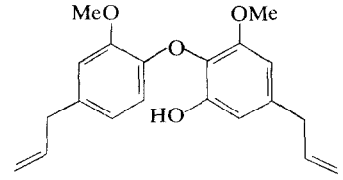
2a R = H
2b R = Ac

Dehydrodieugenol-B (**2a**) was recognized as an isomer of **1a** by high resolution MS. The oxygen and allyl substitution of the aromatic rings was assigned by 270 MHz ^{1}H NMR and confirmed by double irradiation. An allylmethoxybenzene was identified as the major fragment by high resolution MS. Its formation is best explained by a 1,6-hydrogen rearrangement, which requires a free hydroxyl to be situated vicinal to the bridge position of the trioxygenated ring. Only two structures, **2a** and **3a**, are compatible with these results. Acetylation of the hydroxyl in **3a** would be

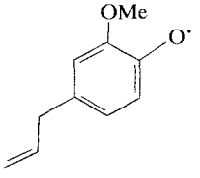
*Part LIX in the series "The Chemistry of Brazilian Lauraceae". For Part LVIII see ref. [1].

† Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel.

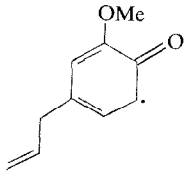
‡ Instituto de Química, Universidade de São Paulo, c.p. 20780, 05508 São Paulo, SP, Brazil.



3a



4



5

expected to shift at least the *ortho*-hydrogen signal about 0.3 ppm to lower field. As the observed shifts are relatively slight (−0.02 and −0.12 ppm), however, both hydrogens probably keep a *meta*-relation with the hydroxyl, and **2a** is the correct representation.

The mesomeric oxidized eugenol radical **4↔5** would account for the biosynthesis of both dehydrodieugenol (**5**+**5**→**1a**) and dehydrodieugenol-B (**4**+**5**→**2a**).

EXPERIMENTAL

Isolation of the constituents. A specimen from a small island of the lower Rio Negro, Amazonas, was collected and identified by Prof. K. Kubitzki, Hamburg. Voucher: Herbarium INPA, Manaus, 58576. A wood sample gave 0.8% of essential oil. Another sample (722 g) was percolated with EtOH giving an extract (46 g). The $CHCl_3$-soluble part (25 g) was chromatographed on silica (400 g). Petrol, C_6H_6 and EtOH in the following proportions 1:0:0, 9:1:0 to 7:3:0, 1:1:0, 0:1:0, 0:98:2 eluted, respectively, terpenes (2.3 g), eugenol (0.7 g), sitosterol (0.3 g) and a mixture (10 g), aliphatic ester (40 mg) and a glycoside (43 mg). The latter two fractions were identical to analogous fractions from *Endlicheria anomala* Nees (Lauraceae) [10] and were not further characterized. The mixture was crystallized from EtOH to **1a** (5.3 g). The mother liquor was evapd and the residue chromatographed on alumina. Petrol eluted **1b** (2.8 g) and an additional product, which upon prep. TLC (Al_2O_3, petrol) gave **1b**, **2a** (25 mg) and aliphatic oil (30 mg).

Dehydrodieugenol (**1a**). Mp and lit. [7] mp 106–107°. Identified by direct comparison with a synthetic sample. *Methyl ether* (**1b**), **1a** (120 mg), Me_2SO_4 (3 ml), dry K_2CO_3 (250 mg) and dry Me_2CO (30 ml) were heated under reflux (5 hr). Work-up gave **1b** (100%), identical with the natural product below. Detectable ^{1}H NMR amounts of dimethyl ether were not produced, even upon extension of the reflux time to 10 hr.

O-Methyldehydrodieugenol (**1b**). Oil, λ_{max}^{MeOH} nm: 270 inf., 283 (ε 4200, 6500); ν_{max}^{film} cm^{-1}: 3450, 1642, 1592, 1497, 1471, 1429, 1282, 1250, 1159, 1070, 935. ^{1}H NMR (60 MHz, $CDCl_3$) : δ 3.33 (*d*, J = 7 Hz, $2CH_2$), 3.60 (*s*, OMe), 3.86 (*s*, 2 OME), 4.8–5.3 (*m*, 2 CH_2), 5.7–6.4 (*m*, 2 CH), 6.63 and 6.70 (2 *s*, 4 ArH). MS (*m/e*): 340 (100%) M$^+$, 178 (4), 177 (3), 164 (8), 163 (5). Acetate (**1c**). Oil, ν_{max}^{film} cm^{-1}: 1767, 1639, 1587, 1471, 1429, 1294, 1220, 1163, 1075, 1031, 939, 870. ^{1}H NMR (60 MHz, CCl_4): δ 2.0 (*s*, OAc), 3.4 (*d*, J = 7 Hz, 2 CH_2), 3.5 (*s*, OMe), 3.83 (*s*, 2 OMe), 4.9–5.3 (*m*, 2 CH_2), 5.5–6.3 (*m*, 2 CH), 6.59 and 6.66 (2 *d*, J = 2 Hz, 2 ArH), 6.72 (*s*, 2 ArH).

Dehydrodieugenol-B (**2a**). Oil, λ_{max}^{MeOh} nm: 275 infl., 285, 325 infl. (ε 9050, 9200, 5000); ν_{max}^{film} cm^{-1}: 3460, 1667, 1592, 1508, 1456, 1422, 1267, 1212, 1134, 1091, 1038, 998, 921. ^{1}H NMR (60 MHz, CCl_4+$CDCl_3$): δ 3.21 and 3.33 (2 *d*, J = 7 Hz, 2 CH_2), 3.81 and 3.85 (2 *s*, 2 OMe), 4.9–5.2 (*m*, 2 CH_2), 5.7–6.2 (*m*, 2 CH), 6.25 and 6.38 (*d*, J = 2 Hz, 2 ArH), 6.71 (*s*, 3 ArH). MS (*m/e*): 326.1520 (100%, $C_{20}H_{22}O_4$ requires 326.1518) M$^+$, 177 (8), 167 (60), 164 (7), 163 (9), 149 (19), 148.0809 (60%, $C_{10}H_{12}O$ requires 148.0888), 147 (17), 133 (8), 131 (10), 117 (14). Acetate (**2b**). Oil, ν_{max}^{film} cm^{-1}: 1773, 1684, 1605, 1511, 1462, 1434, 1364, 1269, 1193, 1100, 1042, 1011, 918. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.24 (*s*, OAc), 3.25 and 3.37 (2 *d*, J = 6.5 Hz, 2 CH_2), 3.81 and 3.82 (2 *s*, 2 OMe), 5.0–5.1 (*m*, 2 CH_2), 5.8–6.1 (*m*, 2 CH), 6.27 and 6.50 (2 *d*, J = 1 Hz, 2 ArH), 6.70 (*dd*, J = 1.5, 8 Hz, ArH), 6.79 (*d*, J = 1.5 Hz, ArH), 6.87 (*d*, J = 8 Hz, ArH).

Acknowledgement—The authors are indebted to Dr. P. M. Baker, NPPN, Universidade Federal do Rio de Janeiro, for high resolution mass spectra.

REFERENCES

1. Ferreira, Z. S., Gottlieb, O. R. and Roque, N. F. (1980) *Biochem. Syst. Ecol.* **8,** 51.
2. Guenther, E. (1950) *The Essential Oils*, Vol. IV, p. 199. Van Nostrand, New York.
3. Mez, C. (1889) *Jahrbuch des Koeniglichen botanischen Gartens und des botanischen Museums zu Berlin*, Vol. 5, p. 250. Gebrueder Borntraeger & Eggers, Berlin.
4. Mors, W. B., Magalhães, M. T. and Gottlieb, O. R. (1959) *Perf. Essent. Oil Rec.* **50,** 26.
5. Gottlieb, O. R. and Magalhães, M. T. (1960) *Perf. Essent. Oil Rec.* **51,** 18.
6. Gottlieb, O. R., Fineberg, M. and Magalhães, M. T. (1962) *Perf. Essent. Oil Rec.* **53,** 219, 299.
7. Holloway, D. M. and Scheinmann, F. (1973) *Phytochemistry* **12,** 1503.
8. Cousin, H. and Hérissey, H. (1908) *Bull. Soc. Chim. Fr., Ser.* 4 **3,** 1066.
9. Fujita, Y. and Shigenoi, J. (1966) *Nippon Kagaku Zasshi* **87,** 1002; *apud Chem. Abstr.* **65,** 18450.
10. Diaz, A. M. P. de, Diaz, D., P. P., Ferreira, Z. S., Gottlieb, O. R., Lima, R. A. de and Cavalcante, S. de H. (1977) *Acta Amazonica (Manaus)* **7,** 292.