Phytochemistry, 1977, Vol. 16, pp. 773–774. Pergamon Press Printed in England.

SESQUITERPENES FROM ESSENTIAL OIL OF *AMYRIS BALSAMIFERA*

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(*Revised received* 29 *December* 1976)

Key Word Index—*Amyris balsamifera*; Rutaceae; essential oil; sesquiterpenes; 10-epi-γ-eudesmol; α-agarofuran; 4-hydroxydihydroagarofuran; valerianol; β-eudesmol; elemol.

Abstract—Six sesquiterpenes were isolated and identified from the essential oil of the wood of *Amyris balsamifera* (Rutaceae): 10-epi-γ-eudesmol, α-agarofuran, 4-hydroxydihydroagarofuran, valerianol, β-eudesmol, elemol.

INTRODUCTION

Amyris balsamifera L. (Rutaceae) or West Indian Sandal Wood is a very common tree growing in Haiti. The essential oil prepared by distillation of the wood is used as a perfume fixative in soaps [1]. The composition of this oil has been studied since the beginning of the century but the results remain confused. Thus β-caryophyllene [2], cadinene [3], cadinols [4,5] have been reported in this oil. When the earlier results were published it was almost impossible to separate the different constituents of the oil and this fact encouraged us to re-examine this oil using modern methods.

RESULTS

Our results differ completely from all previously published works. Thus no cadinane skeleton sesquiterpene was found. However six unreported sesquiterpenes, representing about 70% of the oil were isolated and identified: 10-epi-γ-eudesmol (**1**), α-agarofuran (**2**), 4-hydroxydihydroagarofuran (**3**), valerianol (**4**), β-eudesmol (**5**) and elemol (**6**).

These sesquiterpene series are as far as we know original in the Rutaceae family [6]. Only elemol was reported in orange and grapefruit oil [7,8].

EXPERIMENTAL

Mps were taken after recrystallization from CH_2Cl_2 on a Reichert microscope. Optical rotations were recorded in $CHCl_3$. IR spectra were recorded in $CHCl_3$. NMR spectra were determined at 60 MHz in $CDCl_3$ containing TMS as internal standard. TLC was run on Si gel plates (Merck HF 254). After spraying with a 0.1% soln of berberin hydrochloride in EtOH, the products were observed under UV (366 nm). GLC employed FID and glass columns (1.5 m × 3 mm) packed with either 1% SE-30 or 1% OV-17 (temp. programmed 100–300° at 6°/min). GLC–MS was carried out on a LKB 9000 S mass spectrometer at an ionizing energy of 70 eV. The separation was carried out on a glass column (4 m × 5 mm) packed with 1% Dexsil. The tertiary alcohols (20 μg) dissolved in dry Py (3 μl) were silylated with BSTFA (6 μl) at 80° for 2 hr in a sealed glass container (40 × 1.5 mm). Column chromatography (Si gel) of the essential oil (5 g, commercial sample supplied by the IDAI, Institut de développement agricole et industriel, Port aux Prince, Haiti) gave by elution with *n*-hexane containing an increasing ratio of C_6H_6 successively less polar compounds (380 mg), α-agarofuran (**2**) (140 mg), 10-epi-γ-eudesmol (**1**) (600 mg), a mixture of valerianol (**4**), β-eudesmol (**5**) and elemol (**6**) (2700 mg), and finally 4-hydroxydihydroagarofuran (**3**) (43 mg). An aliquot (500 mg) of the mixture of **4**, **5** and **6** was separated by column chromatography on Si gel–$AgNO_3$ (10:1): **4** (240 mg), **5** (70 mg) and **6** (185 mg) were successively eluted with cyclohexane–EtOAc (98:2), cyclohexane–EtOAc (9:1) and EtOAc.

10-Epi-γ-eudesmol (**1**). $[\alpha]_D$, NMR and IR similar to literature [9]. MS (of TMSi derivative) *m/e* (rel.int.): 279 (M^+-Me, 1), 204 (42), 189 (30), 161 (28), 131 (100), 73 (70). In order to confirm the structure, **1** (11 mg) was treated with a soln of *p*-nitroperbenzoïc acid (40 mg) in $CHCl_3$ (2.5 ml) during 12 hr at room temp. [10]. 4-Hydroxydihydroagarofuan **3** (6 mg) was obtained after purification by TLC (cyclohexane–EtOAc (8:2), R_f = 0.33) and characterized (NMR, IR, mp).

α-Agarofuran (**2**). $[\alpha]_D$, NMR and IR similar to literature [9,11]. MS *m/e* (rel.int.): 220 (M^+, 53), 205 (19), 202 (13), 92 (100).

4-Hydroxydihydroagarofuran (**3**). Mp, $[\alpha]_D$, NMR and IR similar to literature [9,12]. MS (of TMSi derivative), *m/e* (rel. int.): 310 (M^+, 3), 295 (3), 238 (19), 223 (17), 205 (11), 43 (100).

Valerianol (**4**). After Si gel–AgNO3 chromatography, valerianol was contaminated with a minor unidentified alcohol. An aliquot (43 mg) of this mixture dissolved in $CHCl_3$ (500 μl) was acetylated at room temp. during 6 hr with Ac_2O (50 μl) containing *p*-toluene sulfonic acid (50 μg) [13]. The acetates were separated by TLC (cyclohexane–EtOAc 95:5) to give pure valerianyl acetate (14 mg, R_f = 0.45) and a mixture of valerianyl acetate and the unknown acetate.

Valerianyl acetate. Oil. NMR: δ = 0.88 (3H, *d*, *J* = 4 Hz), 0.91 (3H, *s*), 1.40 (6H, *s*), 1.97 (3H, *s*), 5.35 (1H, *m*). MS *m/e* (rel. int.): 204 (M^+-AcOH, 29), 189 (20), 161 (100), 135 (34).

Valerianyl acetate dissolved in dry Et_2O was reduced with $LiAlH_4$ at room temp during 2 hr. Valerianol (**4**) was recovered in the usual way [14] and purified by TLC (CH_2Cl_2, R_f = 0.28).

Valerianol (**4**). Mp, $[\alpha]_D$, NMR and IR identical to the literature [15]. MS (of the TMSi derivative), *m/e* (rel. int.): 279 (M^+-Me, 1), 204 (9), 189 (4), 161 (10), 131 (100).

β-eudesmol (**5**). Mp, $[\alpha]_D$, NMR and IR similar to the literature [16,17]. MS (of the TMSi derivative), *m/e* (rel.int.): 279 (M^+-Me, 1), 204 (0.2), 189 (0.7), 131 (100), 75 (18), 73 (38).

Elemol (**6**). Mp, $[\alpha]_D$, NMR and IR similar to the literature [18,19]. MS (of the TMSi derivative) *m/e* (rel.int.): 279 (M^+, 0.2), 204 (0.6), 189 (1), 131 (100), 75 (26), 73 (45).

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Phytochemistry, 1977, Vol. 16. pp. 774–776. Pergamon Press. Printed in England.

INHALTSSTOFFE AUS *GYNOXYS*- UND *PSEUDOGYNOXYS*-ARTEN*

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(*Eingegangen* 20 *August* 1976)

Key Word Index—*Gynoxys sancto antonii*; *Pseudogynoxys engleri*; *P. sonchoides*; Compositae; new furanoeremophilanes; new polyenes; chemotaxonomy.

Abstract—Five new furanoeremophilanes have been isolated from *Gynoxys sancto antonii*, while two *Pseudogynoxys* species yield three new polyenes. The chemotaxonomic aspects are discussed.

EINLEITUNG

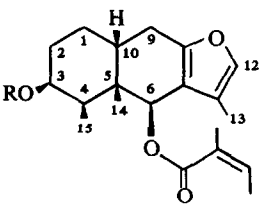
Vertreter der südamerikanischen Gattungen *Gynoxys* und *Pseudogynoxys* (Tribus Senecioneae, Subtribus Seneciinae [1]) sind bisher noch nicht auf ihre Inhaltsstoffe untersucht worden. Wir haben daher drei in Ecuador heimische Arten untersucht, um festzustellen, ob ihre Inhaltsstoffe Anhaltspunkte über die verwandtschaftlichen Beziehungen dieser Gattungen zu den europäischen und südafrikanischen Gattungen der Subtribus Seneciinae erkennen lassen.

DISKUSSION UND ERGEBNISSE

Die Wurzeln von *Gynoxys sancti antonii* Hieron, enthalten in Spuren den Polyinkohlenwasserstoff **1** [2] sowie zwei Furanoeremophilan-Derivate, deren Konstitutionen sich eindeutig aus den spektroskopischen Daten und dem Ergebnis der partiellen Verseifung des gemischten Diesters ergeben.

Es handelt sich um die *cis*-ring-verknüpften Diester **2** und **3**. Derartige Diester haben wir schon früher aus Othonna-Arten, ebenfalls zum Subtribus Seneciinae gehörend, isoliert [3, 4].

$H_3C\,CH{=}CH[C{\equiv}C]_2[CH{=}CH]_2(CH_2)_4CH{=}CH_2$ **1**
trans *trans, trans*



2: R = COCHMe = CHMe (*tr*)
3: R = COCH = CMe_2
4: R = H

Die oberirdischen Teile enthalten dagegen Germacren D (**5**) [5] sowie ebenfalls ein schwer trennbares Diestergemisch. Eine genaue Analyse der NMR-Spektren zeigt, daß wahrscheinlich die Furanoeremophilane **6–8** vorliegen. Bemerkenswert ist die gegenüber **2** und **3** geänderte Konfiguration an C-3, die klar aus den NMR-Spektren an der Lage und den beobachteten Kopplungen zu erkennen ist (vgl. 3).

Die Wurzeln und auch die oberirdischen Teile von *Pseudogynoxys sonchoides* (HBK) Cuatr. enthalten weder Furanoeremophilane noch Acetylenverbindungen. Dagegen findet man als Hauptinhaltsstoff einen Polyenaldehyd mit der Summenformel $C_{18}H_{26}O$. Das UV-Spektrum zeigt, daß ein konjugiertes Tetraen, und das IR-Spektrum, daß ein konjugierter Aldehyd vorliegt. Das ^{1}H-NMR-

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