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STRUCTURE AND STEREOCHEMISTRY OF THE DITERPENES OF *HYMENAEA COURBARIL* (*CAESALPINIOIDEAE*) SEED POD RESIN

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Abstract—The isolation and structure of four new bicarbocyclic diterpenes from seed pod resin of Guadeloupe-grown *Hymenaea courbaril* is described. The diterpene composition of this resin is more highly rearranged than those isolated from the trunk resin of the same tree. Cyclosativene, caryophyllene, α-himachalene, selina-4(14),7(11)-diene were identified as major sesquiterpene components while β-bourbonene, calarene, selina 4(14),7-diene, humulene, δ-cadinene, α-calacorene and α-muurolene were identified as minor components.

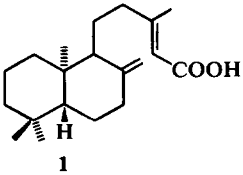
Hymenaea and *Trachylobium* are closely related large tropical trees with wide distribution. Damage of the trunks of these trees results in the exudation of resin which is commercially important as a base for varnishes, copal. Investigations[1-4] of these resins have revealed they are comprised principally of diterpenes such as copalic acid (1) possessing labdane skeletons. The leaf pocket resin of *T. verrucosum*, Oliv. and *H. courbaril*, L. contains major amounts of caryophyllene and α- and β-selinene with minor amounts of α-cubebene, α-copaene, β-copaene, α- and β-humulene, γ-muurolene and δ-cadinene.[5,6]

Based on the similarity of trunk resin and leaf pocket resin compositions as well as morphological and chromosomal characters, Langenheim has recently proposed reclassification of *T. verrucosum* as a *Hymenaea*.[7] The resin extracted from the seed pods of Madagascar grown *T. verrucosum* was found to contain principally tetra- and pentacyclic diterpenes possessing the (—) kaurene (2) and (—) trachylobane (3) skeletons.[8] Also found in this resin was a small amount of zanzibaric acid (4′) which possesses the (—) labdane skeleton, the principal skeleton of the trunk resin constituents. The present investigation is of the resin extracted from the seed pods of Guadeloupe-grown *H. courbaril.* In contrast to the seed pod resin of *T. verrucosum* of Madagascar, the resin under investigation contained principally bicyclic diterpenes possessing rearranged (—) labdane skeletons.

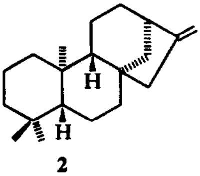
The resin, obtained by benzene extraction of the pulverized pods, was esterified with diazomethane and subjected to GLPC analysis on a glass QF-1 column. Only four components (**5**, **7**, **8** and **13**) in the diterpene region were evident. Under the conditions of this analysis diterpene alcohols, diols (e.g., oliveradiol) ketones and keto esters (e.g., **9**) were stable and observable. Separation of the crude extract by column, thin layer and preparative gas chromatography yielded **5**, **7**, **8**, and **13** and several sesquiterpenes.

Structure of ester **5**. The spectral properties of **5**, $C_{21}H_{32}O_2$, suggested a bicarbocyclic diterpene ester. The mass spectral fragmentation pattern revealed the same major fragments as those obtained from methyl communate (4, R=H).[9]

The NMR spectrum showed the presence of one carbomethoxy group, two Me groups at quaternary positions (δ 0·70 and 1·14) and seven vinylic hydrogens. The vinylic portion of the NMR spectrum of **5** was indistinguishable from that of sclarene but



1



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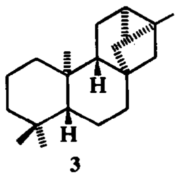

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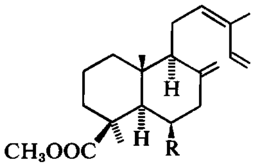

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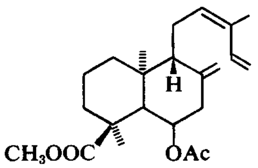
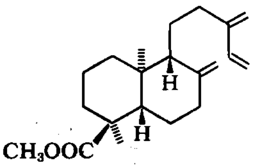
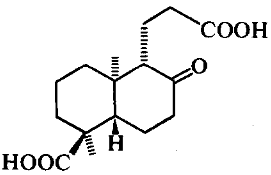


4′



5

differed significantly from those of *cis* and *trans*-biformenes.[10] This comparison suggested the presence of a diene-contining side chain with a structure identical to that in sclarene. Also suggested by this comparison was the presence of an *exo* methylene group. The suspected unsaturation was confirmed by ozonolysis of **5**. Alkaline hydrogen peroxide treatment gave a keto-dicarboxylic acid **6** with m.p. and optical rotation identical to that reported for this compound.[11] This degradation, with the spectral observations, establishes the structure and stereochemistry of **5**.



6

Structure of esters **7** *and* **8**. Esters **7** and **8** were separable only by preparative gas chromatography. On a QF-1 packed column **7** was eluted prior to **8**, suggesting the former was more fully saturated. The NMR and mass spectra of **7** indicated that it was a mono-olefinic bicarbocyclic diterpene ester. The NMR spectrum showed the presence of two Me's in quaternary positions (δ 0·88, 1·11), two tertiary Me groups (δ 0·70, J = 7·0 Hz; δ 0·95, J = 6·5 Hz), two carbomethoxyl groups (δ 3·63) and one vinyl hydrogen (δ 5·37). Reduction of **7** with LAH gave a diol in which one hydroxymethylene function appeared as a sharp AB quartet. This pattern and the chemical shift observed for these resonances were consistent with an equatorial hydroxymethylene function attached to a fused decalin system.[12] Also evident in the NMR spectrum of the diol derived from **7** was a triplet (δ 3·60, J = 6·8 Hz) due to hydroxymethylene hydrogens produced upon reduction of the second ester. This ester is therefore attached to a methylene (as in $—CH_2-COOCH_3$).

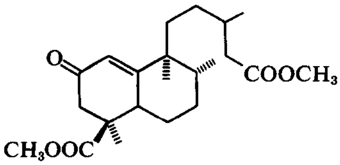
The NMR spectrum of the diacetate of the diol derived from **7** revealed the presence of an AB quartet again in the rather narrowly defined region expected of an equatorial acetoxymethylene function attached to a decalin system.[12]

Treatment of **7** with sodium chromate in acetic acid gave an α,β-unsaturated ketone **9** (λ_{max} 237 nm, $\epsilon = 3·4 \times 10^4$). The substitution surrounding this functional group was deduced to be as in partial structure **A** by calculation of the expected UV maximum[13] and comparison of the change of chemical shift experienced by the vinyl hydrogen of **7** upon oxidation ($\Delta\delta$ 0·42) with those experienced by the α(δ 0·32) and β($\Delta\delta$ 1·38) hydrogens upon oxidation of cyclohexene to cyclohexenone.

Partial structure **A** was extended to **B** upon the observation of base exchange of a two hydrogen AB quartet (δ_A 2·24, δ_B 2·72, J = 16 Hz), an exchangeable one hydrogen quartet (δ_C 3·04, J = 5, 11·5 Hz) and the vinyl hydrogen (δ_D 5·79).

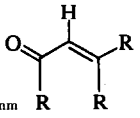
Benzene solvent induced shift experiments indicated[14] the exchangeable AB quartet was geminal to a CO in a cyclohexenone ring ($\Delta\delta_A$ $CDCl_3—C_6H_6 = 0$, $\Delta\delta_B$ $CDCl_3—C_6H_6 = +0·25$). This and the observation that exchangeable H_c is coupled to two adjacent hydrogens in a non-equivalent fashion allowed extention of partial structure **B** to C_1–C_4.

Evidence for the spatial relationship between the trisubstituted cyclohexenyl double bond of **7** and its two quaternary methyls was deduced from examination of the NMR spectra of the isomeric epoxides (**10** and **11**) obtained from reaction of **7** with *p*-nitroperbenzoic acid. The NMR spectrum of the less polar epoxide (**10**) revealed the high field quaternary methyl (δ 0·88) of **7** moved to δ 0·65 in the epoxide whereas the other Me resonance remained relatively unchanged. The NMR spectrum of **11** revealed both quaternary Me's (δ 0·88 and δ 1·11) of **7** at higher field (δ 0·70 and δ 1·01). These observations place the quaternary Me not as-

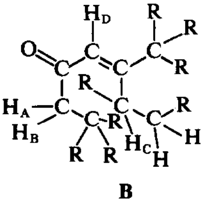


9

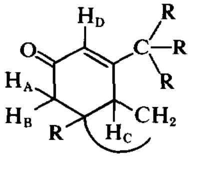
$\lambda^{Calcd^{13}}_{max\ 239nm}$



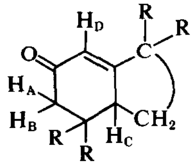
A



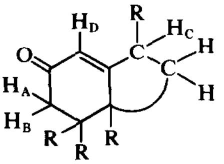
B



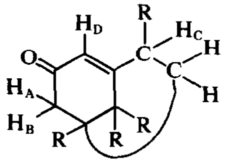
C$_1$



C$_2$



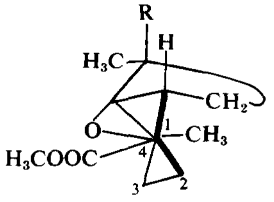
C$_3$



C$_4$

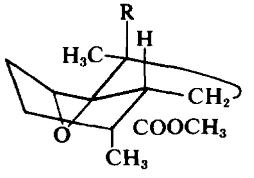
sociated with the carbomethoxyl-bearing carbon in the shielding cone of the epoxide functions in **10** and **11**, while the quaternary Me associated with the carbomethoxy group is placed in the shielding cone of the epoxide function of **11**.

The partial structure most consistent with this spatial relationship is C$_2$ wherein the quaternary Me not associated with the carbomethoxyl function is in a *peri* relationship to the epoxide ring as in **D**.[15]

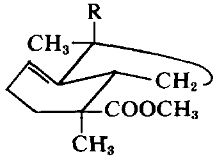


10

D

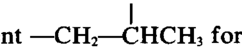


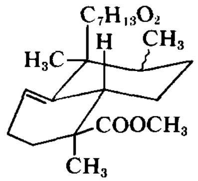
11



E

Additional evidence for a *peri* relationship between the high field quaternary Me and the unsaturation of **7** was obtained by NOE.[15] Thus irradiation at the frequency of the high field quaternary methyl of **9** (derived from **7** by allylic oxidation) resulted in a 35 ± 10% increase in the integrated intensity of the vinyl hydrogen signal (relative to both internal chloroform and the carbomethoxyl resonances). This is expected only if the quaternary Me has close steric proximity to the vinyl hydrogen. The above implied extention of the partial structure of **7** to **E**.

Structure **E** accounts for $C_{12}H_{17}O_2$ of $C_{22}H_{36}O_4$ in **7**. The mass spectrum of **7** reveals a base peak at *m/e* 235 which corresponds to loss of $C_7H_{13}O_2$[*] (*m/e* 129). The next most prominent peak is at *m/e* 175 and is produced by loss of $HCOOCH_3$ (*m/e* = 60) from the *m/e* 235 ion as evidenced by a metastable ion at 130. Considering the most probable point of fragmentation of partial structure **E** to be the allylic center containing the quaternary Me, if rupture occurred eliminating the ion of *m/e* 129, the formula of the remaining fragment would be $C_{15}H_{23}O_2$ of which $C_{12}H_{17}O_2$ is deduced. The remaining undetermined portion of the *m/e* 235 fragment is C_3H_6. Of the possible structural arrangements for this fragment  $—CH_2—\overset{|}{C}HCH_3$ formulation is compatible with the presence of one of the two tertiary Me doublet resonances in the NMR spectrum of **7**. Scrutiny of the mass spectrum of **9** reveals a major ion (*m/e* 249) also produced by loss of a m = 129 fragment. The *m/e* 249 ion subsequently eliminates $HCOOCH_3$ to yield a fragment *m/e* 189 containing the oxygenation additional to **9**. Ions at *m/e* 161, 122, 121 and *m/e* 41 are considered to originate from *m/e* 189 via retro-Diels-Alder reactions (Scheme 1) and require the tertiary Me of the C_3H_6 fragment to be adjacent to the quaternary Me. Structure **E** may thus be extended to **F**.



F

The above assignments were corroborated by mass spectral analysis of the diethylene ketal derivative of **9**. In this derivative, **10**, ionization occurred primarily at the ketal function followed by loss of dioxane then loss of the side chain and retro-Diels-Alder reactions to give *m/e* 121 as the dominant ion in the spectrum.

Considerable but unfruitful effort was invested in attempting to extend the conjugation of ring A of **7** to ring B. It was presumed that definitive evidence as to the location of the secondary Me group in ring B could be obtained if this could be achieved.

The stereochemistry of this tertiary Me was deduced from benzene solvent induced NMR shifts observed for **9** and by Eu(fod)$_3$ induced shifts[17] of epoxides **10** and **11**. In the former experiment it was found that both quaternary Me's and one of the two tertiary Me resonances shifted by nearly identical amounts to higher field as the solvent was changed from chloroform to benzene. Although the quater-

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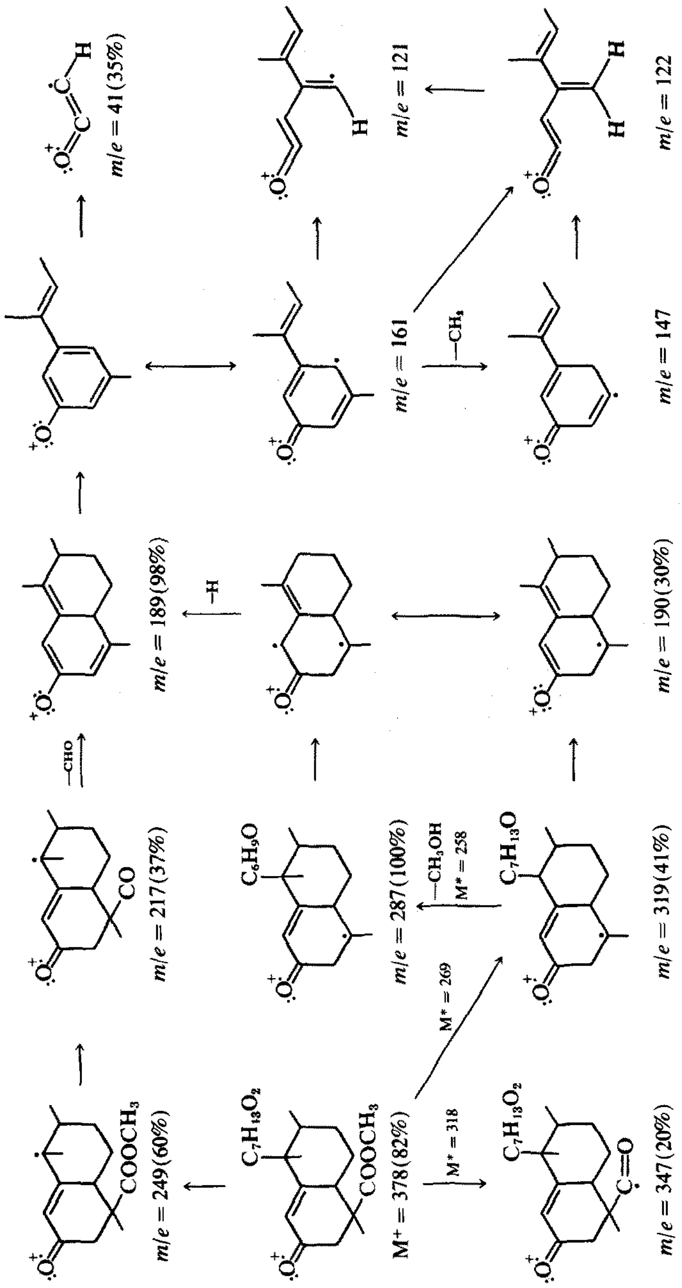
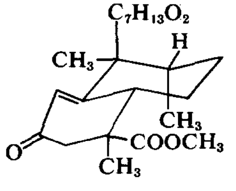
[*] This composition was supported by the observation of a fragment at *m/e* 69, i.e. 129—$HCOOCH_3$.



SCHEME 1. Fragmentation pattern of 9

nary Me's have previously been located relatively near the conjugated CO, in order for there to be a distinct upfield shift of a tertiary Me resonance in this experiment, the tertiary Me group must either be sterically near this group or be *axial* in the proposed decalin system. Since the mass spectral cracking pattern placed a tertiary Me at C_8, if it is *axial* it must be α as given in partial structure **G**.

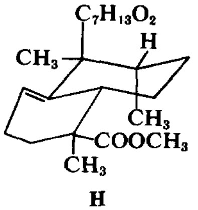


G

Confirming this assignment are the observed rates of change of chemical shifts of the quaternary and tertiary Me resonances upon the addition of Eu(fod)$_3$ to solutions of **7** and its epoxide derivatives **10** and **11**. When Eu(fod)$_3$ was added to solutions of these compounds in carbon tetrachloride in amounts varying from 0·28 to 1·1 molar ratios and the induced NMR shifts of the quaternary and tertiary Me resonances were plotted *vs* [Eu(fod)$_3$]/[Substrate], straight line plots were obtained (Table 1).

It is observed that for **10** the rate of shift of all Me resonances is much greater than for those of **7** or epoxide **11**, supporting the earlier deduction that the epoxide and ester functions are on the same side of the molecule in the former epoxide.*

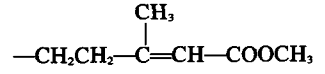
Significantly, when internal comparisons are made, the ratios of the rate of shift of the ring B tertiary Me to the rate of shift of each other Me resonance are greater for **11** than for **10** or **7**. This observation is consistent only with the location of the tertiary Me in ring B nearer the α-epoxide oxygen of **11** than the β-epoxide oxygen of **10**.



H

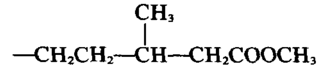
The partial structure, **H**, of **7** deduced at this point, leaves the $C_7H_{13}O_2$ fragment undefined except for the presence of one tertiary Me (>CHMe) and a methylene carbomethoxy function (—CH$_2$-COOMe). The structure of this fragment was deduced by chemical correlation of **7** with a second component of the pod resin. Thus **8**, separable from **7** only by GLPC, exhibited spectra indicating a structure similar to **7** except for the presence of an additional double bond which was conjugated with an ester (λ_{max} 220, $\epsilon = 16{,}300$) and was responsible for the appearance of a vinyl Me doublet (δ 2·19, J = 1·2 Hz) and a vinyl hydrogen (δ 5·73) resonance. Hydrogenation of **8** with Pd/BaSO$_4$ resulted in the disappearance of the vinyl Me and hydrogen resonance and the formation of a product indistinguishable by NMR, IR, UV and MS from **7**. This establishes **8** as an unsaturated analog of **7** and requires the site of unsaturation to reside in the C_7 fragment. Since reduction of this unsaturation must (a) remove the conjugation with an ester, (b) produce a CH$_2$COOMe function, and (c) produce a —CHMe group in the C_7 fragment, the structure of this fragment in **8** and **7** must be **I** and **J** respectively.

The stereochemistry of the double bond in **I** was determined to be *trans* by comparison of the chemical shift (δ 2·19) of the vinyl Me of **8** with related α,β-unsaturated esters.[18]



$$-CH_2CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-COOCH_3$$

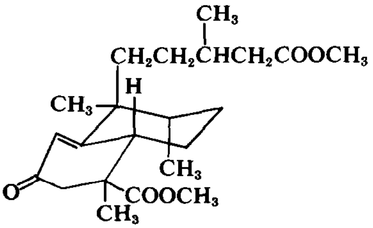
I



$$-CH_2CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}H}-CH_2COOCH_3$$

J

These observations allow formulation of structures for **7** and **8** but do not define the absolute stereochemistry of their decalin rings nor the configuration at C_{13} of **7**. Comparison of the CD curves of **9** and **12** indicated an opposite configuration at C_5. Since **12** is known to be 5α, the hydrogen of **9** (and thus of **7** and **8**) must be 5β. These diterpenes thus belong to the same antipodal class as **5**.



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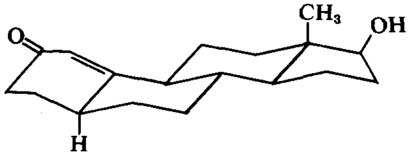

12

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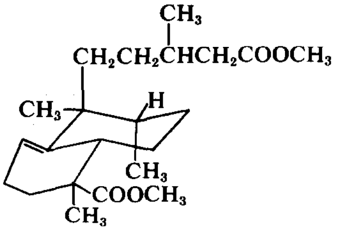
*Close proximity between two or more polar groups contribute to increased ability of the substrate to coordinate with the Eu(fod)$_3$ reagent, resulting in larger shift gradients for the substrate hydrogens.

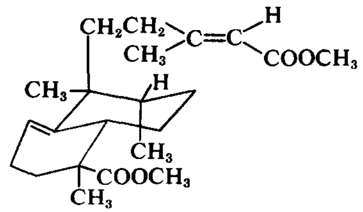
Table 1. Gradients of downfield shift in Hz per mole Eu(fod)$_3$ per mole of substrate and ratio of gradients of methyl groups in compounds **7**, **10** and **11**

Compound	Gradients Downfield shift in Hz $\Big/ \frac{\text{mole Eu(fod)}_3}{\text{mole of substrate}}$									
	C_4—CH_3	C_8—CH_3*	C_9—CH_3	C_{13}—CH_3	C_8—CH_3 C_4—CH_3	C_8—CH_3 C_9—CH_3	C_8—CH_3 C_{13}—CH_3	C_9—CH_3 C_{13}—CH_3	C_4—CH_3 C_{13}—CH_3	C_4—CH_3 C_9—CH_3
7	1·55	0·387	0·75	1·57	0·25	0·52	0·25	0·48	0·99	2·07
10	4·08	1·00	1·90	2·65	0·25	0·53	0·38	0·72	0·54	2·14
11	1·83	0·70	0·96	1·50	0·38	0·73	0·48	0·64	1·22	1·90

*C_8—CH_3 = tertiary Me ring in **B**.



7



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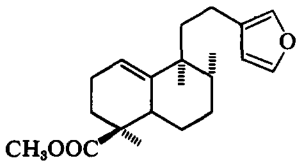

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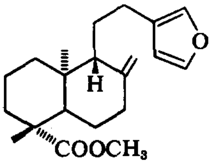

14

Structure of ester **13**. The spectral properties of **13** ($C_{21}H_{30}O_3$) suggested a bicyclic diterpene possessing a β-substituted furan ring. The NMR of **13** revealed the presence of two quaternary Me groups (δ 0·97, δ 1·13), a tertiary Me doublet (δ 0·83, J = 6·5 Hz), one carbomethoxy function (δ 3·62); and a vinyl hydrogen (δ 5·37). Three one-hydrogen triplets at δ 6·15, 7·10 and 7·15[19] and IR absorptions[20] at 1560, 1510 and 875 cm^{-1} indicated the presence of a β-substituted furan.

The mass spectral fragmentation pattern of **13** suggested the furan ring was attached to the side chain of a rearranged labdane skeleton. Thus while intense ions at *m/e* 81 and *m/e* 95 are also prominent in the mass spectrum of methyl daniellate (**14**),[9] the base peak of the mass spectrum of **13** is *m/e* 235 (as was observed for **7** and **8**), indicating particularly facile cleavage of the furan-containing side chain. The stereochemistry and absolute configuration of **13** are assumed to be identical to those of **5**, **7** and **8**.

Sesquiterpenes. Sesquiterpene hydrocarbons of the seed pod resin were identified by comparative gas chromatographic retention indices.[21,22] The crude resin was found to contain cyclosativene, caryophyllene, α-himachalene, seline-4(14), 7(11)-diene as major sesquiterpene components and β-bourbonene, calarene, selina-4(14),7-diene, humulene, δ-cadinene, α-calacorene and α-muurolene as minor components, (Table 2).

DISCUSSION

There is a structural difference between the diterpene constituents of the trunk resin of *H. courbaril* and those of the resin extracted from the seed pods. The relative stereochemistry at C_5, C_9 and C_8 deduced in **7** and **8** is that expected of a backbone rearrangement of a (-)labdanyl precursor with the relative stereochemistry of **5**. Although several rearranged labdane diterpenes have been isolated[23,24,25] from Amherstiae with skeletons related to that encountered in **7** and **8**, the only previously reported occurrence of diterpenes with this skeleton was in the roots of *Adenochlaena siamensis*, Ridl. (Euphorbiaceae).[26]

Langenheim[4] has found remarkable consistency with respect to skeleton in the diterpenes that comprise the trunk resins of *Hymenaea*. The only *Hymenaea* previously investigated with respect to

Table 2. Sesquiterpene hydrocarbons in seed-pod resin of *Hymenaea courbaril*

Compound	Percentage*
A	3·3
B	0·85
C	1·2
Cyclosativene	17·3
β-Bourbonene	1·1
D	0·5
Caryophyllene	13·5
E	1·0
Calarene	0·4
F	1·8
Humulene	1·6
Selina-4(14),7-diene	0·3
α-Himachalene	13·5
G	1·2
α-Muurolene	6·1
δ-Cadinene	5·2
H	3·98
Selina-4(14),7(11)-diene	16·2
I	7·4
J	1·6
K	1·6

*Mean of two determinations; % of sesquiterpene fraction is approximately 10% of total terpene composition.

its seed pod resin composition is *H. verrucosa* Gaertn. (previously *T. verrucosum* Oliv.).[7]

Analysis of the esterified (diazomethane) crude extracts of the seed pods of several *Hymenaea* supplied by Professor Langenheim reveals the presence of major quantities of labdane and rearranged labdane compounds.

Sesquiterpenes are considered to be derived from cyclization of *trans,trans* and *trans,cis*-farnesyl pyrophosphates to intermediates which further cyclize eventually giving known compounds. The major sesquiterpenes in *H. courbaril* leaf pocket resin are of the type derived from the *trans,trans*-farnesol path (2·5:1) with 1/10 (selinenes) and 1/11 (caryophyllene, humulene) initial cyclizations being approximately equally represented. Only the 1/10 route (cadinene, murrolene, copaenes) was encountered in the cyclizations proceeding from the *trans,cis*-farnesyl precursor.

The sesquiterpenes found in the seed pod resin are distributed between those derived from the *trans,trans* precursor and *trans,cis* precursor in an approximate 3:4 ratio. Those derived from the *trans,trans* precursor were produced from 1/10 (selinadienes) and 1/11 (humulene, caryophyllene) cyclization in approximately equal amounts. The sesquiterpenes derived from the *trans,cis* precursor are formed via 1/10 (muurolene, cadinene, cyclosativene) and 1/11 (himachalene) cyclization (2:1). The primary difference between the leaf pocket and seed pod sesquiterpenes is the presence of 1/11 cyclization products from the *trans,cis* precursor.

EXPERIMENTAL

IR spectra were obtained neat or with KBr using a Perkin-Elmer 457 spectrophotometer. NMR spectra were obtained at 100 MHz in $CDCl_4$ using TMS as internal standard. Molecular weights and fragmentation patterns: Hitachi Perkin-Elmer RMU-7 double focusing mass spectrophotometer (I.E. = 70 eV).

Extraction of Hymenaea courbaril *seed pods.* Dry seed pods of Guadeloupe-grown *H. courbaril* were pulverized and extracted repeatedly with benzene at r.t. until only minute amounts of extract were obtained. Evaporation of the benzene gave 57 g of dark resin from 950 g pods.

Isolation of resin components. A portion (26 g) of the resin was chromatographed on Silica Gel (500 g). Elution with light petroleum:ether (9:1 to 3:1) gave 8·8 g of a mixture of **5**, **7**, **8** and **13**. Continued elution with ether gave about 15 g of more polar components which are unidentified. The isolated components were further separated by prep TLC on SiO_2/10% $AgNO_3$ eluting with EtOAC:light petroleum (3:7). The least polar, **13** gave $[\alpha]_{\mathrm{D}}^{25^\circ}$ +53° ($c = 0\cdot25$, $CHCl_3$); $\nu_{\max}^{\text{film}}$ 3120, 1725, 1560–1540, 1510, 1255, 1165, 1025, 875 and 780 cm^{-1}. (Found: C, 76·76; H, 9·30. Mol. wt. by m.s. 330. Calcd. for $C_{21}H_{30}O_3$ (330): C, 76·32; H, 9·15%).

The next component to be eluted was **5**; $[\alpha]_{\mathrm{D}}^{25^\circ}$ − 17·5° ($c = 0\cdot4$, $CHCl_3$); $\nu_{\max}^{\text{film}}$ 3080, 2940, 2872, 1726, 1645, 1594, 1444, 1387, 1245, 1199, 1171, 1147, 1101, 989, 891, 759 and 715 cm^{-1}; $\lambda_{\max}$ 226 nm ($\epsilon = 10{,}000$). Found: mol. wt. by mass spec, 316. Calcd. for $C_{21}H_{32}O_2$: mol. wt., 316.

Last to be eluted under these conditions were **7** and **8** which were eluted as a mixture.

Separation of the mixture of **7** and **8** by prep GLC on a 1·5% QF-1 on Chrom. G column at 210° gave **7**; $[\alpha]_{\mathrm{D}}^{25^\circ}$ + 31·4° ($c = 0\cdot77$, $CHCl_3$); $\nu_{\max}^{\text{film}}$ 2940, 1725, 1650, 1250, 1190, 1160, 1150, 1110 and 880 cm^{-1}. (Found: C, 72·59; H, 9·65. Calcd. for $C_{22}H_{36}O_4$ (364): C, 72·49; H, 9·96%). Ester **8** gave $[\alpha]_{\mathrm{D}}^{25^\circ}$ + 0·694° ($c = 0\cdot288$, $CHCl_3$); $\nu_{\max}^{\text{film}}$ 2948, 2872, 1720, 1644, 1225, 1150 and 920 cm^{-1}; $\lambda_{\max}$ 220 nm, $\epsilon =$ 16,354.

GLPC analysis of the crude esterified resin on QF-1 as above with anisoin as an internal standard revealed the only components with retention times longer than those of sesquiterpenes were (in order of elution) **5** (8·3%), **13** (19%), **7** (9%), and **8** (1%).

Ozonolysis of **5**. A soln of 372 mg of **5** in 4 ml EtOAc and 3 ml glacial HOAC was cooled to 0° and a stream of O_3 and O_2 gas was passed through the soln for 2 hr. To the cold mixture was added 5 ml of 10% NaOH aq and 2 ml of 30% H_2O_2. The mixture was allowed to warm to r.t. The soln was kept stirring overnight at r.t. then extracted with ether which was dried over $MgSO_4$ and evaporated to give 369 mg of an oil. Treatment of the oil with ethereal diazomethane (from 1·5 g of nitrosomethyl urea) followed by removal of the ether *in vacuo* gave a viscous gum which was separated by prep TLC on Silica Gel impregnated with 10% $AgNO_3$ to give 94·7 mg of the diester of **6** and an unidentified compound; $\nu_{\max}^{\text{film}}$ 2940, 1710, 1444, 1390, 1250, 965 and 755 cm^{-1}; NMR ($CDCl_3$): δ 0·76 (3H,s), δ 1·19 (3H,s), δ 2·33 (2H; AB quartet, J = 6,6,13 Hz), δ 3·65 (3H,s), δ 3·69 (3H,s).

A soln of 94 mg of the keto diester in 6 ml of 12% methanolic KOH was refluxed for 14 hr. The MeOH was evaporated *in vacuo*, the residue diluted with water and extracted with ether to remove traces of non-acidic material. The aqueous soln was acidified and then extracted with ether. The solvent was removed and the residue triturated with dry ether to yield 74 mg of **6**, crystallized from light petroleum:EtOAc (40:60) to give **6**, m.p. 211–212°, $[\alpha]_{\mathrm{D}}^{25^\circ}$ + 11·67° ($c = 0\cdot48$ in MeOH); $\nu_{\max}^{\text{film}}$ 3500 (broad), 2940, 2874, 1700, 1450, 1390, 1372, 1248, 1046 and 962 cm^{-1}; NMR ($CDCl_3$): δ 0·76 (3H,s), δ 1·19 (3H,s), δ 2·33 (2H,q). Lit.[11] m.p. 211–212°, $[\alpha]_{\mathrm{D}}^{28} = +11\cdot6^\circ$ ($c = 4\cdot05$ in MeOH).

Reduction of **7** *with LAH.* To a soln of 100 mg of **7** in 25 ml ether was added 100 mg LAH. The soln was refluxed for 2 hr then worked up in the usual manner. Chromatography of the crude reduction product on SiO_2/10% $AgNO_3$ showed two components which were separated by prep TLC. The principal product (58 mg) was a diol. NMR ($CDCl_3$): δ 0·78 (3H, d, J = 6 Hz); δ 0·87 (3H, d, J = 6 Hz); δ 0·84 (3H,s); δ 0·87 (3H,s); δ 3·34 (2H, AB quartet, J = 10·5 Hz); δ 3·60 (2H, t, J = 6·8 Hz); δ 5·30 (1H, t, J = 3·5 Hz). Found: mol. wt. by mass spec, 309. Calcd. for $C_{20}H_{37}O_2$: mol. wt., 309.

Acetylation of diol from **7**. The diacetate was formed by allowing the diol to stand at r.t. with Ac_2O in pyridine for 3 days. It was isolated by prep TLC as an oil, $\nu_{\max}^{\text{film}}$ 1750, 1250, and 1140 cm^{-1}; NMR ($CDCl_3$): δ 0·81 (3H, d, J = 6 Hz); δ 0·87 (6H,s); δ 0·88 (3H, d, J = 6 Hz); δ 2·03 (6H,s); δ 3·85 (2H, AB quartet, J = 10·5 Hz); δ 4·09 (2H, t, J = 6·8 Hz) and δ 5·32 (1H, t, J = 3·5 Hz). Found: mol. wt. by mass spec, 393. Calcd. for $C_{24}H_{41}O_4$: mol. wt., 393.

Allylic oxidation of **7**. A soln of 300 mg of **7** in 1·5 ml AcOH and 2 ml benzene containing 2·5 ml Ac_2O, 150 mg of Na_2CrO_4, 250 mg of NaOAc was stirred for 3 days at 45°. The solvent was evaporated *in vacuo* and the residue chromatographed directly on 30 g of SiO_2/10% $AgNO_3$.

Elution with 250 cc of 10% ether: 90% light petroleum gave 30 mg of unreacted **7**. Elution of the column with 250 cc of 3:7 mixture of ethyl ether: light petroleum gave 203 mg **9**; ν_{max}^{film} 1740, 1680, and 1620 cm^{-1}; NMR ($CDCl_3$): δ 0·80 (3H, d, J = 7 Hz), δ 0·95 (3H, d, J = 6 Hz), δ 0·99 (3H,s), δ 1·23 (3H,s), δ 2·48 (2H, AB quartet, J = 16, 16, 28 Hz), δ 3·02 (1H, AB quartet, 5, 5, 11·5 Hz), δ 3·60 (6H,s), δ 5·79 (1H,s); $[\alpha]_D^{25°}$+105° (c = 1·1, $CHCl_3$). (Found: C, 70·00; H, 8·92. Mol. wt. by mass spec: 378. Calcd. for $C_{22}H_{34}O_5$ (378): C, 69·81; H, 9·05%).

Preparation of the diethylene ketal derivative of **9**. A soln of 18 mg (0·048 mmole) **9**, 0·07 ml diethylene glycol (3 drops) and 4 ml p-toluenesulfonic acid in 17 ml dry benzene was refluxed for 70 min. Benzene was then slowly distilled, fresh benzene being added to the mixture at frequent intervals to maintain the initial volume. After 1·5 hr a total of 40 ml distillate had been collected. The benzene soln containing the product was washed with conc $NaHCO_3$ aq then with H_2O until neutral. The soln was then dried over $CaCl_2$ and evaporated to give 8·7 mg of the ketal; ν_{max}^{film} 2940, 2880, 1730, 1670, 1460, 1435, 1378, 1238, 1150, 1010, 948, 850 and 730 cm^{-1}. Found: mol. wt. by mass spec, 466. Calcd. for $C_{26}H_{42}O_7$: mol. wt. 466.

Epoxidation of **7**. A soln of 325 mg of **7** and 200 mg p-nitroperbenzoic acid in 15 ml $CHCl_3$ was allowed to stand at r.t. for 1 hr. After this time TLC analysis showed that the alkene was consumed. Prep TLC of the crude mixture (SiO_2/10% $AgNO_3$) gave 107 mg **10** and 92 mg of **11** (more polar) as oils. **10**; $[\alpha]_D^{25°}$−15° (c = 1·4, $CHCl_3$); NMR ($CDCl_3$): δ 0·65 (3H,s), δ 0·98 (3H, d, J = 6 Hz), δ 1·16 (3H, d, J = 11 Hz), δ 1·20 (3H,s) δ 2·92 (1H, t, J = 2·5 Hz), and δ 3·63 (3H,s). Found: mol. wt. by mass spec, 380. Calcd. for $C_{22}H_{36}O_5$: mol. wt. 380.

Compound **11**; $[\alpha]_D^{25°}$+57° (c = 0·9, $CHCl_3$); NMR ($CDCl_3$): δ 0·70 (3H,s), δ 0·93 (3H, d, J = 6 Hz), δ 0·99 (3H, d, J = 6 Hz), δ 1·01 (3H,s), δ 2·94 (1H, d, J = 4 Hz), and δ 3·68 (6H,s). Found: mol. wt. by mass spec, 380. Calcd. for $C_{22}H_{36}O_5$: mol. wt. 380.

Hydrogenation of **8**. A soln of 50 mg of **8** in 20 ml EtOAc was shaken with 30 mg of Pd/$BaSO_4$ under 50 p.s.i.g. H_2 at r.t. for 18 hr. After this time, excess Pd/$BaSO_4$ was filtered and the solvent evaporated *in vacuo* to give 30 mg of a compound whose IR, NMR and mass spectra were identical with those of **7**.

Isolation and identification of sesquiterpenes. During the chromatography of the crude esterified resin a fraction was eluted between **13** and **4** which GLPC, NMR and MS (mol. wt. 202–204) revealed to contain numerous sesquiterpenes. These components were identified (Table 2) by determination of their Kovats' indices (Table 3) on three columns (Apiezon L, DEGS and SE30) using α-copaene and γ-cadinene as standards.[21]

Analyses were performed using a Varian-Areograph 1400 unit on 20′ × $\frac{1}{8}$″ stainless steel columns introducing the sesquiterpenes as 5% solns in n-decane.

Table 3. Kovats' indices of sesquiterpenes in seed pod resins of *Hymenaea courbaril*

	Kovats' indices*					
	Apiezon L, 155°C		DEGS, 160°C		SE30, 130°C	
Compounds†	observed	Lit.	observed	Lit.	observed	Lit.[21]
A	1363				1348·3	
B	1383·4					
C	1403·7					
Cyclosativene	1411·4	1411·9	1683·9	1684		
β-Bourbonene	1418·2	1418·3			1388	1386
D	1441·4					
Caryophyllene	1451·5	1451·7			1417·4	1417·5
E	1459·2					
Calarene	1466·8	1466·0			1435·1	1435
F	1479·7					
Humulene	1489·1	1487·2			1448·9	1446·8
Selina-4(14)-7-diene	1493·4	1491·9	1852·2	1852·5		
α-Himachalene	1507·3	1508·0			1872	1870
G	1519·1					
α-Muurolene	1531·7	1531·3			1492·7	1495
δ-Cadinene	1547·3	1546·4			1504·6	1504
H	1555·5	**1554·9‡**				
Selina-4(14)-7(11)-diene	1572·8	1572	2019·3	2018		
I	1579·2	1580§				
J	1603·3					
K	1611·4					

*These indices are an average of three determinations and the precision are ±0·9.

†Compounds A–K are unidentified.

‡Kovats' index of γ-cadinene.[21]

§Kovats' index for selina-3,7(11)-diene.[21]

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