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NATURAL AND THERMAL ISOMERS OF METHYL *TRANS*-COMMUNATE

A CHEMICAL, SPECTROSCOPIC AND MECHANISTIC CONSIDERATION OF THE ASSIGNED STRUCTURES

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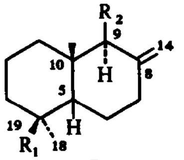
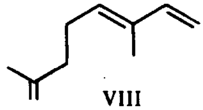
Abstract—A new diterpene acid, isolated as its methyl ester from *Callitris columellaris* F. Muell., is shown to be $\Delta^{13(17)}$-communic acid. Another new isomer of communic acid is shown to result from thermal rearrangement of *trans*-communic acid methyl ester on gas chromatography, and is tentatively assigned the structure methyl labda-8(14)-*trans*-11(12)-*cis*-13(15)-trien-19-oate on the basis of spectroscopic and mechanistic considerations.

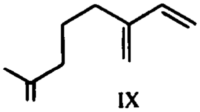
THE terpenoids of Australian white cypress pine (*Callitris columellaris* F. Muell.), and of the oleoresin exuded by the tree, have been examined by a number of workers.[1–4] In the course of other work we have conducted a detailed investigation of the fresh bark and sapwood and of the oleoresin of this species. While many of the findings represent only confirmation of previous work, we wish to report here the existence of two new isomers in the communic acid group. One of these is evidently of natural occurrence, while the other is shown to arise by thermal isomerization of one of the main diterpenoid components, *trans*-communic acid.



I — VII



VIII



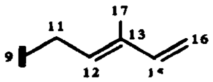
IX

R_2

I COOH

II COOMe

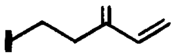
R_2



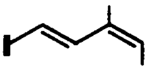
III COOH

IV COOMe

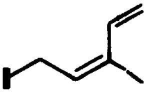
V CH_2OH



VI COOMe



VII COOMe



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Earlier workers[5] had elucidated the structure of the sidechain at the 9-position in *trans*-communic acid (I) by comparison of the UV and PMR data with those for the corresponding acylic monoterpene *trans*-α-ocimene (VIII). In the case of the new isomer, a similar correlation was shown to exist with α-myrcene (IX). Since the comparison of the PMR spectrum of the new ester with those of several[5,10,11] suitable 10β-, 9α-H, 5α, 4β-COOMe models indicated identity of the carbocyclic moiety with that of I, the structure IV was assigned tentatively. Reduction of the ester with LAH converted it to the corresponding alcohol, which was identified as $\Delta^{13(17)}$-communol (V) by direct comparison with an authentic sample obtained by dehydration of torulosol.[6]

Thermal isomerization of methyl trans-*communate*

Methyl *trans*-communate could be isolated by direct crystallization of the crude bark esters. Attempts to purify this ester by gas chromatography resulted not only in the usual losses due to polymerization, but also (at elevated temps) in isomerization to a new ester, isomeric with the starting material. As in the case of IV, we were able to assign a tentative structure (VI) on the basis of spectroscopic evidence.

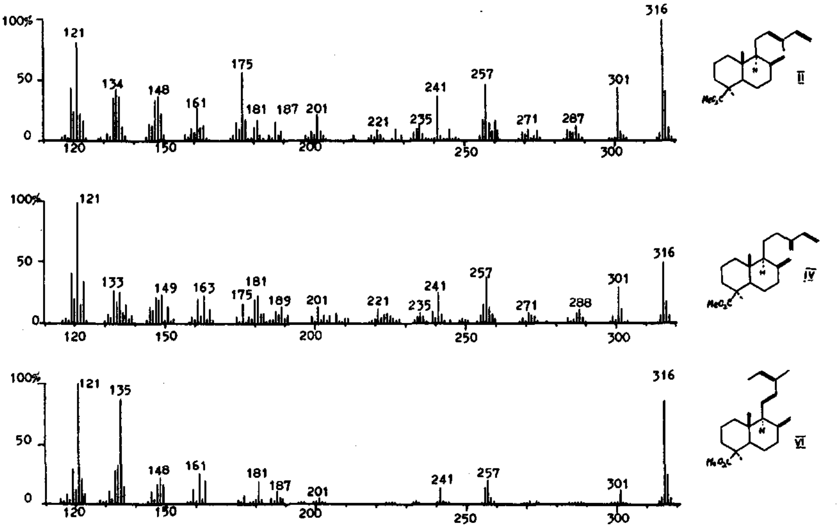
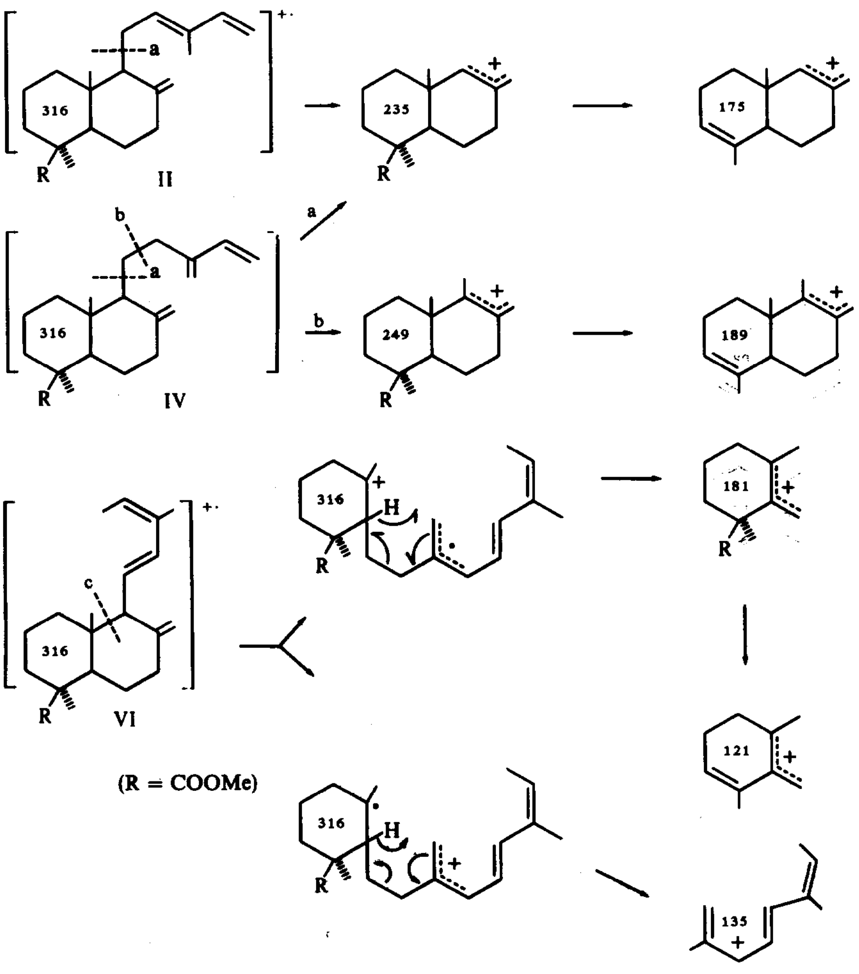


FIG. 1.70 ev Mass Spectra of Methyl Communate Isomers.

The mass spectrum showed the fragmentation pattern characteristic of a carbodicyclic diterpenoid methyl ester, $C_{21}H_{32}O_2$, with a C_8–C_{14} double bond,[7] while the PMR spectrum indicated that the carbocyclic moiety of II remained unaltered in the transformation. The UV absorption (λ_{max} 236·5, log ε 4·34) of the isomerization product was found to coincide well with that of 2,6-dimethyl-*trans*-4-*cis*-6-octatrien-1,4,6. (X, λ_{max} 236, log ε 4·36[8]). In the IR spectrum the olefinic region of the isomer was virtually superposable on that of X; a single band in the 1550–1700 cm^{-1} region, a feature which appears to distinguish X from other acyclic monoterpenes containing the conjugated diene structure,[9] was also characteristic of the isomerized ester. The PMR spectrum tended to confirm the structural assignment VI, showing five olefinic protons* between τ 3·40 and 5·60, a broad Me singlet at τ 8·23 (C_{13}-Me) and a Me doublet at τ 8·36 (C_{15}-Me).

The mass spectra of the three isomers II, IV and VI (Fig. 1) are predictably similar. The structures advanced are consistent with the relative differences observed in ions *m/e* 175 and 189. The former arises from allylic cleavage of the 9–11 bond (... a, Chart I) followed by loss of the ester moiety,[7] whereas the latter arises from cleavage of the 10–11 bond (... b, Chart I). Both ions are of comparable abundance in the mass spectrum of IV, while *m/e* 175 predominates (about 7:1) in that of II. Neither ion is significant in the spectrum of VI, where the preferred cleavage is that of the 9–10 bond (... c, Chart I). In this last case the positive charge would be expected to be shared between C_9 (doubly allylic) and C_{10} (tertiary) resulting in ions at *m/e* 135, 181 and 121



(R = COOMe)

CHART I

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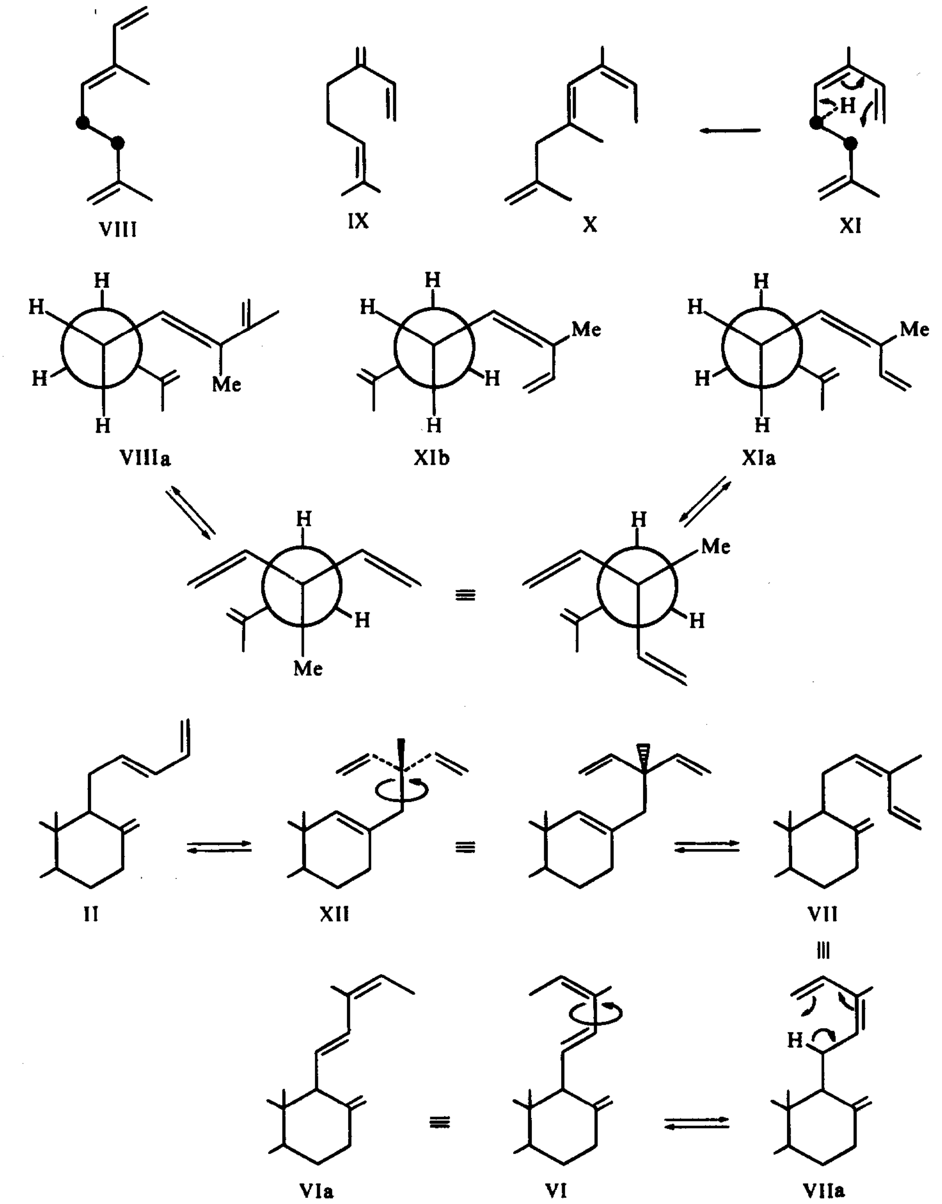
* The spectrum was computer-accumulated, and resolution was not adequate for a full analysis of these small signals.

as shown. In the spectra of II and IV, on the other hand, the *m/e* 316 → 181 → 121 pathway should predominate; in fact *m/e* 135 is much reduced in these spectra.



Mechanism of thermal rearrangement

cis-α-Ocimene (XI) undergoes[8] 1,5-sigmatropic H-shift to X on heating, whereas the isomeric *trans*-α-ocimene (VIII) and α-myrcene (IX) cannot attain the conformation required for the suprafacial shift. Both are stable to thermal rearrangement,[8] and it might be expected that the diterpene analogues II and IV would show similar behaviour. While this is true in the case of methyl $\Delta^{13(17)}$-communate (IV), methyl *trans*-communate (II analogous to VIII) undergoes thermal isomerization to VI.

A Cope rearrangement is possible in both the acyclic terpenes VIII and XI. Newman projections of the transition states (VIIIa and XIa) reveal that, in fact, a *double* Cope rearrangement would be the most likely consequence, and that this could only result in an apparent interconversion of VIII and XI. Such a series of reactions evidently does not occur in VIII and XI, being disfavoured by the conformational mobility* of the acyclic systems. The analysis does, however, reveal a pathway between methyl *trans*-communate (II) and its thermal isomer VI, as outlined in Chart II. The greater rigidity of the diterpenoid system would make the Cope rearrangement much more favourable than in the corresponding acyclic series. It is proposed that the *trans*-ester is equilibrated with methyl *cis*-communate (VII) through the first Cope product XII, and the *cis*-ester then undergoes a 1,5-H-shift to produce VI. As in the acyclic case, we assume that the Cope intermediate XII would be inherently less stable than either II or VII and would thus occur only as a transient intermediate. Inspection of Dreiding models indicates that the *trans*-isomer (II), experiencing less steric interactions, would be thermodynamically favoured over the *cis*-isomer (VII), and therefore would normally predominate in the equilibrium mixture. However, because of these same unfavourable interactions in VII, it would be expected to adopt the conformation VIIa, minimizing the interactions between C_{10}-Me and C_{14} with the terminal atoms ($C_{15, 16, 17}$) of the sidechain. This is the required conformation for the suprafacial 1,5-H-shift leading to VI, and this reaction should now compete favourably with reversal of the Cope transformation. Since reversal of the sigmatropic shift (VII → VI) is also possible, we must seek some reason for the survival of VI as the final product in what is essentially a series of reversible reactions. This may be found in the $C_{11, 16}$ interaction in VI, which can be minimized by rotation around the $C_{12, 13}$ bond to the conformer VIa. In this case steric hindrance is not quite so extreme, but it will be noted that the C_{11}-C_{16} interaction is avoided in VIa. A similar experimental situation arises in the acyclic monoterpene X—the product of the 1,5-H-shift (X) evidently does *not* undergo reversion to *cis*-α-ocimene. Although it is possible that the greater stability of VI and X is in some part connected with the higher degree of substitution of the double bonds, the steric arguments are probably of significance, particularly in the more rigid carbocyclic species VI.

EXPERIMENTAL

PMR spectra were recorded at 60 MHz using $CDCl_3$ solns with TMS as an internal standard. IR spectra were measured as liquid films or in CCL_4. UV spectra were taken in 90% EtOH. Mass spectra were obtained on A.E.I. MS9 and MS10C2 instruments.

Preparation of extractives. The timber and oleoresin of *Callitris columellaris* was collected at Beni State Forest near Dubbo in northwestern New South Wales. A fine sawdust (3 mm mesh) of both bark and sapwood was obtained using a Wiley mill. Extraction of the fresh sawdust with light petroleum gave viscous oils in 4·10% (bark) and 0·15% (sapwood) yields. The oleoresin dissolved completely in diethyl ether. Excess hexane was then added to each extract to remove polymeric material.[1, 3] The NaOH-soluble acids were extracted and methylated with ethereal diazomethane at 0°; yields of polymeric, acidic and

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* The relevant conformations are XIb (H-shift) and XIa (Cope).

neutral fractions are recorded. Steam-volatile oils were obtained by distillation of the sawdust or oleoresin in all-glass apparatus.

COMPOSITION OF EXTRACTS

	Per cent of total extract		
	Bark	Sapwood	Oleoresin
Polymer	5·7	0·5	54·4
Acids	74·6	36·0	35·2
Neutral	19·7	63·5	10·4

Identification of constituents. Colourless needles of II could be precipitated in low yield from 30% methanolic solns of the methylated fractions. Preparative gas chromatography on a 6′ 20% Carbowax ($\frac{3}{8}$ o.d.) column and micro-preparative GLC on 12′ 20% Carbowax 20M ($\frac{3}{16}$″ o.d.), 12′ 20% LAC-446 ($\frac{3}{16}$″ o.d.) and 5′ 20% SE 30 ($\frac{1}{4}$″ o.d.) columns, either individually or in combination, were used to obtain pure, other components from the various extracts. II and methyl sandaracopimarate could not be satisfactorily separated by GLC. To overcome this II was removed from a sample, containing both compounds, as the di-acid of its Diels-Alder adduct with maleic anhydride.[9] The neutral fraction then yielded pure methyl sandaracopimarate on work up. All constituents identified, other than IV, yielded analytical data which could be readily assigned to a known compound; direct comparisons with authentic samples corroborated each assignment.

(i) *Steam-volatile oils.* The analysis of the sapwood volatile fraction was consistent with that for the heartwood by Rudman.[12] The oils of the bark and oleoresin were extremely similar, both being rich in α-pinene with lesser amounts of other mono- and sesquiterpenoids; of these only camphene, β-pinene, limonene, 1,8-cineole, *p*-cymene, camphor, isoborneol and methyl perillate were identified with certainty. Isoborneol however, was later shown to be an artefact of distillation.

(ii) *Acids.* All terpenoid acid constituents, with the exception of III, characterized in this investigation have been previously reported as constituents of either the sapwood[13] or oleoresin[1–4] of *Callitris columellaris*. In addition to these however, the sapwood was found to contain a series of fatty acids, C_{16} and C_{18} compounds predominating; palmitic acid was identified as the major component. The acid compositions of the bark, sapwood and oleoresin are tabled.

COMPOSITION OF C. COLUMELLARIS ACID METHYL ESTERS

Methyl Sandaracopimarate taken as 100 parts. Retention volumes (R) are relative to methyl sandaracopimarate on Carbowax 20M.

	Composition			
Compound	Bark	Sapwood	Oleoresin	R
Methyl citronellate	—	35	—	0·34
Methyl palmitate	—	91	—	0·58
Methyl $\Delta^{13(17)}$-communate	37	65	—	0·86
Methyl *trans*-communate (II)	23	75	—	1·00
Methyl sandaracopimarate	100	100	100	1·00
Methyl isopimarate	10	23	34	1·09
Methyl 4-epidehydroabietate	84	104	189	1·18

(iii) *Methyl $\Delta^{13(17)}$-communate* (IV). Gas chromatography on the 6′ Carbowax column yielded IV as an oil: Mol. wt. 316·2411 ($C_{21}H_{32}O_2$ requires: 316·2402); λ_{max} 226 mμ (log ε 4·28); ν_{max} (film) 2075 w, 1800 w, 1790 w, 1725 s, 1645 m, 1597 m, 1150 s, 997 m, 900 s cm^{-1}; PMR spectrum: τ 9·53, 8·88 (C_{10}, C_4 methyls), 6·42 (C_4 carbomethoxy), 5·38, 5·13 (C_{14} protons), 5·03 (C_{17} protons), 3·41–5·08 (ABX multiplet, H_A (C_{16}) 4·98, H_B (C_{16}) 4·84, H_X (C_{15}) 3·63, J_{AB} 1, J_{AX} 11, J_{BX} 17 hz). IV (0·04 g) was treated with LAH in the usual way, yielding V as an oil pure by chromatography: λ_{max} 226 mμ (log ε 4·35); ν_{max} (film): 3400 s, 3085 w, 1780 w, 1642 m, 1597 m, 1022 s, 986 m, 890 s, cm^{-1}; PMR spectrum: τ 9·34, 9·02 (C_{10}, C_4 methyls), 6·40 (AB quartet, C_{19} protons; $J = 11$ hz), 5·42, 5·13 (C_{14} protons), 5·00 (C_{17} protons), 3·35–5·05 (ABX multiplet, H_A (C_{16}) 4·94, H_B (C_{16}) 4·78, H_X (C_{15}) 3·57, J_{AB} 1, J_{AX} 11, J_{BX} 17 hz). The mass spectrum showed a parent ion at *m/e* 288 ($C_{20}H_{32}O$ requires *m/e* 288). The assigned structure V was confirmed by direct comparison with an authentic sample prepared by the acetic acid–acetic anhydride dehydration of torulosol.[9]

Rearrangement of methyl-trans-*communate* (II). A sample of pure II (0·005 g in 20 µl acetone) was injected into the 12′ Carbowax column (245°, block and injection port at 300°), and the eluted material condensed; two re-injections yielded the crude artefact VI, corresponding to the only peak now apparent on the chromatogram. The peak with retention time consistent with II was now absent. Four such runs resulted in the collection of 0·003–0·004 g of crude material. Contamination with column bleed necessitated further chromatography on the SE 30 column at 215°. This yielded 0·001–0·002 g pure artefact VI; ν_{max} (film) 1782 w, 1725 s, 1648 m, 1225 m, 1155 s, 975 m, 892 s, 825 w cm^{-1}; PMR spectrum: τ 9·40, 8·81 (C_{10}, C_4 methyls), 6·41 (C_4 carbomethoxy). Other spectral data has already been given. The retention volume relative to II on the 12′ Carbowax was measured as 0·70. No rearrangement of II was observed at a column temp of 230° with the block and injection port temps at 225°. An F. and M. 500 gas chromatograph with a thermal conductivity detector was used to observe the rearrangement.

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REFERENCES

[1] R. M. Carman and H. C. Deeth, *Austral. J. Chem.* **20**, 2789 (1967).
[2] L. J. Gough, *Chemy Ind.* 2059 (1964).
[3] L. J. Gough, *Tetrahedron Letters* 295 (1968).
[4] L. J. Gough, private communication.
[5] T. Norin, *Acta Chem. Scand.* **19**, 1020 (1965).
[6] V. P. Arya, H. Erdtman and T. Kubota, *Tetrahedron* **16**, 255 (1961).
[7] C. R. Enzell and R. Ryhage, *Arkiv für Kemi.* **23**, 367 (1965).
[8] G. Ohloff, J. Seibel and E. Kovats, *Liebigs Ann.* **675**, 83 (1964).
[9] B. M. Mitzner, E. T. Theimer and S. K. Freeman, *App. Spect.* **19**, 169 (1965).
[10] L. Mangoni and M. Belardini, *Gazz. Chim., Ital.* **94**, 1108 (1964).
[11] M. Sumimoto, Y. Tanaka and K. Matsufuji, *Tetrahedron* **20**, 1427 (1964).
[12] P. Rudman, *Holzforschung* **18**, 116 (1964).
[13] V. M. Trikojus and D. E. White, *J. Proc. Roy. Soc. N.S.W.* **66**, 284 (1932).