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STUDIES IN SESQUITERPENES—XX

ACETOXYMETHYLATION OF LONGIFOLENE*

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Abstract—Longifolene in Prins reaction with formaldehyde yielded the expected ω-acetoxymethyl longifolene, which was transformed into a number of interesting derivatives. Configuration of the Prins product has been arrived at by NMR measurements. The UV absorption of these derivatives show a considerable bathochromic shift with respect to those in the camphene series and this could be attributed to the slight twisting of the ethylenic linkage in longifolene and its derivatives.

THE olefin-aldehyde condensation (Prins reaction[1])[2] is a reaction of technical value and the products from β-pinene-formaldehyde are useful perfumery synthetics. Other monoterpenes condensed with formaldehyde include camphene[3] and Δ^3-carene.[4] In connection with the exploration of the possible outlets for the industrial utilization‡ of longifolene, the chief sesquiterpene of Indian turpentine oil (from *Pinus longifolia* Roxb.), its acetoxymethylation and some further transformations of the product, have been studied. Apart from a casual mention of cedrene[1,5] giving rise to homocedrenol by the Prins reaction, longifolene would be the first sesquiterpene olefin to have been studied in this condensation in a detailed manner.

Condensation of longifolene with paraformaldehyde in acetic acid at reflux gave a liquid product in a yield of 60% besides recovered hydrocarbon (25%); from the distillation residues a small yield of a high boiling fraction, which has not been fully characterized, could also be obtained. The structure (I)[6] for the main Prins product follows from its reactions discussed below.

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‡ Sponsored by the Essential Oil Research Committee, India.

[1] H. J. Prins, *Proc. Acad. Sci. Amsterdam* **22,** 51 (1919).

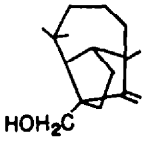
[2] E. Arundale and L. A. Mikeska, *Chem. Rev.* **51,** 505 (1952).

[3] G. Langlois, *Ann. Chim.* **12,** 265 (1919); *Chem. Abstr.* **14,** 2777 (1920).

[4] G. Ohloff, H. Farnow and W. Philipp, *Liebigs Ann.* **613,** 43 (1958).

[5] H. J. Prins, *J. Chem. Soc.* **118,** (I), 42 (1920); *Chem. Abstr.* **14,** 1662 (1920).

[6] Recently K. Nagai, I. Ogura and G. Takeda [*Nippon Kagaku Zasshi* **81,** 1715 (1960); *Chem. Abstr.* **56,** 12951f (1962)] have also investigated this condensation under essentially similar conditions and, have assigned the structure:

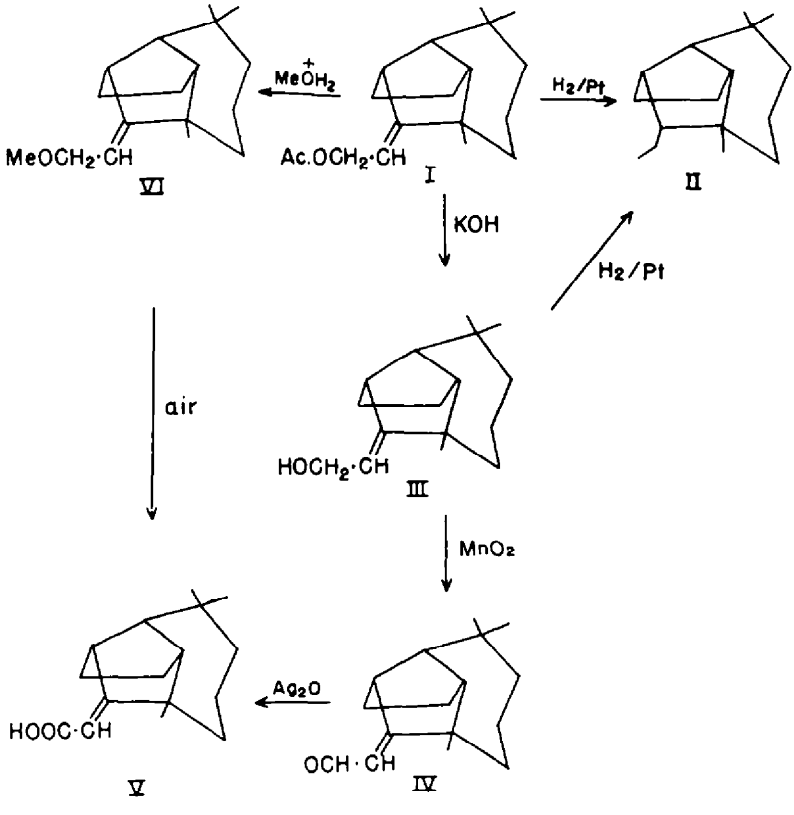


to the alcohol derived from the acetate. As would be clear from the present communication this structure is untenable.

The Prins product analysed for $C_{18}H_{28}O_2$ and gave a yellow colour with tetranitromethane. In the IR it (neat) displays bands for acetoxyl (1737, 1230 cm^{-1}) and C=C unsaturation (1670 cm^{-1}). Catalytic hydrogenation over platium oxide in acetic acid medium resulted in considerable hydrogenolysis to yield a saturated hydrocarbon, homolongifolane, in 69% yield. This finding fixes the olefinic group in an allylic position with respect to the acetoxyl. On the basis of these data and the method of preparation, structure I for the Prins product and II for homolongifolane follow.

The acetate (I) on a mild base hydrolysis yielded the crystalline alcohol (III) in an almost quantitative yield; when the hydrolysis was carried out at reflux, only polymeric material resulted. The unsaturated alcohol is quite labile and on storage at room temperature (25°) deteriorates within a few weeks, a behaviour, characteristic of certain $\beta\gamma$-unsaturated alcohols. This alcohol also, like the acetate, suffered hydrogenolysis during catalytic hydrogenation.

The unsaturated alcohol could be smoothly oxidized to the corresponding solid $\alpha\beta$-unsaturated aldehyde (IV), either with manganese dioxide or low temperature chromic acid oxidation. The product showed light absorption behaviour (ν^{C-H} 2725, $\nu^{C=O}$ 1670, $\nu^{C=C}$ 1625 cm^{-1}; λ_{max}^{EtOH} 253 mμ, ϵ = 15630) expected of $\alpha\beta$-unsaturated aldehydes though the λ_{max} in the UV absorption is at a significantly longer wavelength than is normal (*vide infra*). The aldehyde is sensitive to oxygen and during crystallization is partly converted to the acid V, if sufficient precautions



are not taken. The aldehyde can be readily oxidized to this acid (V) either with silver oxide or by air oxidation catalysed by manganese acetate. This acid was found to be identical with the acid V, earlier prepared by Naffa and Ourisson[7] by the hydrolysis of the carbon tetrachloridelongifolene addition product (VI).

When the acetate (I) was heated with excess of methanol in the presence of sulphosalicylic acid, with simultaneous removal of methyl acetate formed in the exchange reaction, ω-methoxymethyl longifolene (VII) could be obtained in an excellent yield. The product was found to be unstable to oxygen and slowly deposited the acid (V) on exposure to air.[8]

Stereochemistry

Two configurations VII and VIII are possible for the ω-acetoxymethyl longifolene (or its derivatives) and only one of these can represent the Prins acetate, as it yields a single alcohol (crystalline) in almost quantitative yield on base-hydrolysis. As discussed below, a decision in favour of the configuration VII may be made on the basis of NMR data. On the same basis the Prins acetate from camphene may also be assigned the configuration XV.

With this information, consideration of the mechanism for the Prins reaction could lead to a prediction of the configuration assigned to the acetate. The mechanism of acid-catalysed-olefin reaction has been discussed by several authors.[9–13] In the longifoleneformaldehyde condensation, IX should represent the intermediary species, which by proton elimination would yield the product.[14] Elimination of Ha (path a) would lead to VII, whereas path b (elimination of Hb) will result in VIII. Since, Ha and Hb are symmetrically situated with respect to the C . . .$^{+}$OH bond, the distortion of the quasi-four-membered ring, as required for the transition state for the elimination step (antiparallelity of concerned bonds) would be the same for both the paths,

[7] P. Naffa and G. Ourisson, *Bull. Soc. Chim. Fr.* 1075 (1954).

[8] The reaction could be visualized as proceeding through the hydroperoxide → aldehyde → acid.

[9] C. C. Price, *Ind. Eng. Chem.* **40**, 257 (1948).

[10] V. Franzen and H. Krauch, *Chem. Ztg.* **79**, 335 (1955).

[11] E. E. Smissman and R. A. Mode, *J. Amer. Chem. Soc.* **79**, 3447 (1957).

[12] A. T. Blomquist and J. Wolinsky, *J. Amer. Chem. Soc.* **79**, 6025 (1957).

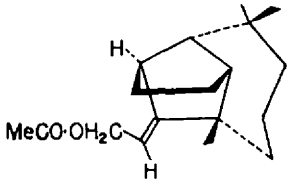
[13] L. J. Dolby, C. N. Lieske, D. R. Rosencrantz and M. J. Schwarz, *J. Amer. Chem. Soc.* **85**, 47 (1963).

[14] In the acid-catalysed condensation of pinene[6] or camphene[9] with formaldehyde no Wagner-Meerwein-type rearrangement has been reported. This strongly suggests that a free carbonium ion mechanism cannot be operative and that the incipient carbonium is at once complexed by the hydroxyl oxygen to a species like IX, which by proton elimination gives the product. This conclusion has been arrived at earlier by others[11,12] on the basis of the exclusive formation of *trans*-isomer of 2-acetoxy methylcyclohexylacetate in a Prins reaction of cyclohexene and formaldehyde.

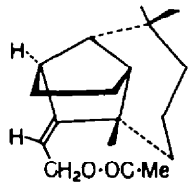
From the known[15,16] chemistry of longifolene, it is clear that the approach of $CH_2^{\oplus}OH$ will be from the less-hindered endo-face[16] as shown in IX. The initial product from IX would be the alcohol, which would then get converted to the acetate. Though in the condensation of longifolene and formaldehyde, no mineral acid or Lewis acid has been used, it has been experimentally demonstrated that the Prins alcohol gets quantitatively acetylated by refluxing with acetic acid under the reaction conditions used for the Prins reaction. However, the product may arise by the direct attack of $CH_2^{\oplus}OAc$ on longifolene, in which case the oxonium cation will form a quasi-six-membered ring,[13] and this species would yield the acetate direct by proton-elimination.

[15] P. Ourisson and G. Ourisson, *Bull. Soc. Chim. Fr.* 1415 (1954).

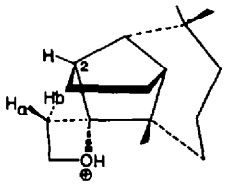
[16] G. Ourisson, *Bull. Soc. Chim. Fr.* 895 (1955).



VII



VIII

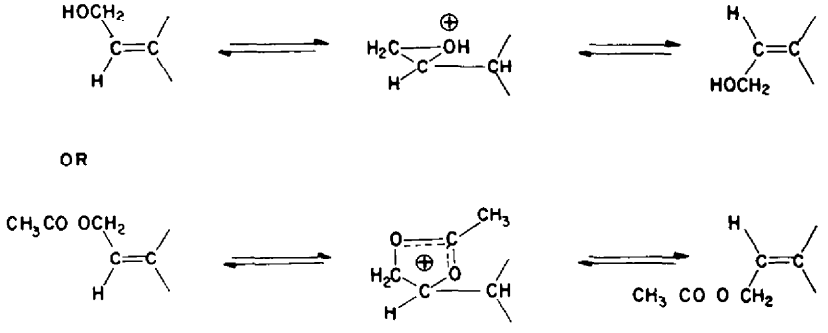


IX

thus precluding any special preference for a particular elimination. However, models reveal that path b may be energetically somewhat less favoured, because in this transition state proton Ha and the lone tertiary proton at C_2 eclipse each other; such a situation does not arise for Ha elimination and this may account for at least some excess of VII over VIII. An exactly similar situation presents itself if we consider the oxonium cation with a quasi-six-membered ring, arising from an attack by $\overset{+}{C}H_2OAc$, rather than $\overset{+}{C}H_2OH$.[14,*]

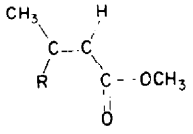
The configuration VII for the ω-acetoxymethyl longifolene was deduced from the proton magnetic resonance (PMR) studies of the ω-methoxy carbonyl longifolene derived from this. It has been clearly demonstrated[17] that in $\alpha\beta$-unsaturated carbonyl compounds, the β-proton or the protons on the β-alkyl substituent are deshielded further if the carbonyl function and these protons are *cis* to each other; the effect has been ascribed to the anisotropy of the carbonyl group. This difference in the chemical shift has been used to differentiate between *cis* (X) and *trans* (XI) isomers of

* It has been pointed out by the referee that the isolated Prins acetate may as well have resulted from a thermodynamic product control, the favoured isomer being the one with the less-hindered CH_2OAc group. Examination of models suggested that steric strain could well be less in the acetate which was isolated. The isomerisation could involve the following processes:

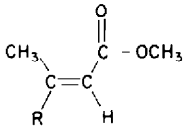


[17] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* pp. 119–125. Pergamon Press, London (1959).

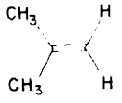
trisubstituted ethylenes,[18–21] The method can be used decisively, when both the isomers are available for a comparative study. In the present case only one isomer was available, and hence recourse had to be made to a comparison with the unsubstituted parent system, i.e. longifolene. A comparison of the chemical shift data[18,22] for



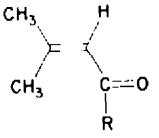
X



XI

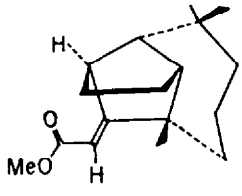


XII

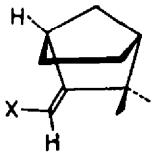


XIII

allylic methyl groups in isobutylene (XII) and the methyl groups in XIII revealed a deshielding to the extent of ~0·4 p.p.m. when the methyl is *cis* to the carbonyl function, as compared to ~0·18 p.p.m. when the methyl is *trans* to the carbonyl group, the deshielding being with respect to the methyl groups in the parent XII. On this basis a minimum 0·4 p.p.m. shift to the lower field strength was to be expected for the ω-methoxy carbonyl longifolene (XIV) as compared to longifolene for the lone allylic proton. Moreover, since in the case of systems like XI and XIII the methyl group has free rotation, the deshielding due to the diamagnetic anisotropy of the carbonyl, will be averaged out over all the three methyl protons. On the other hand in XIV, due to the fixed position of the allylic proton, a much higher deshielding



XIV



XV

effect is to be anticipated. In excellent agreement with this, the shift has been found to be 1·47 p.p.m. (Fig. 1) thus clearly supporting configuration (XIV for ω-methoxycarbonyl longifolene. Table 1 summarizes pertinent PMR data for these and several other ω-substituted derivatives of longifolene; also included are some corresponding camphene derivatives, which also show similar deshielding and consequently must possess the configuration (XV).

[18] L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.* 196 (1958); *J. Chem. Soc.* 2881 (1960).
[19] R. Morris, C. A. Vernon and R. F. M. White, *Proc. Chem. Soc.* 303 (1958).
[20] J. W. K. Burrel, L. M. Jackman and B. C. L. Weedon, *Proc. Chem. Soc.* 263 (1959).
[21] J. A. Elvidge, *J. Chem. Soc.* 474 (1959).
[22] Ref. 15, Table 4.8 on p. 58

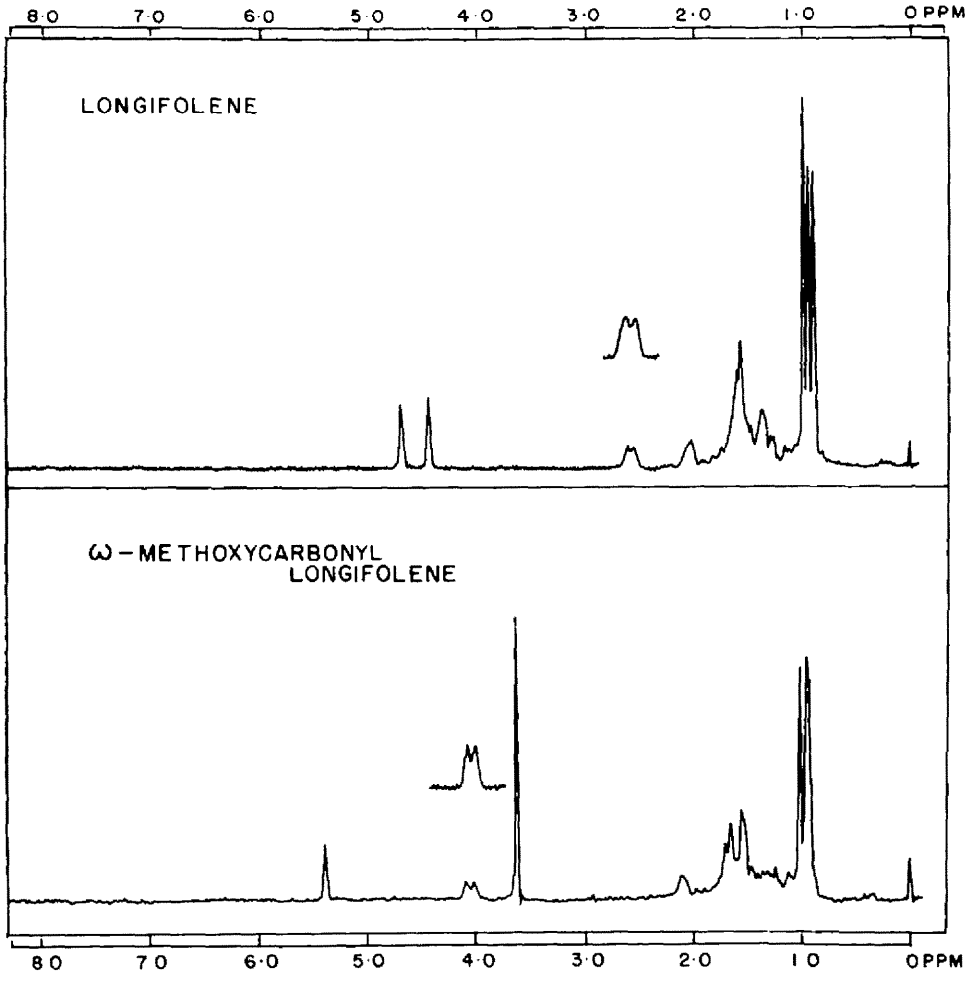


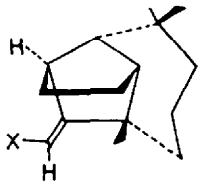
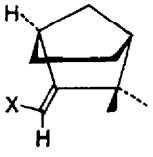
FIG. 1. PMR Spectra of longifolene and ω-methoxycarbonyl longifolene.

Ultraviolet absorption

It has already been mentioned that ω-formyl-longifolene (IV) showed λ_{max}^{EtOH} 253 mμ, which is considerably displaced to the visible, as compared to a value of 244 mμ expected[23] for a cyclopentylidene acetaldehyde. It has been known for sometime now that bicyclo [3,2,1] octane[24–27] and bicyclo [2,2,1] heptane[28–30] derivatives show a bathochromic shift with respect to the corresponding simpler cyclopentane

[23] e.g. L. Dorfman [*Chem. Rev.* **53**, 47 (1953)] reports for λ_{max} an average value of 244 mμ (ε ~ 27,000) for steroidal Δ^{17}-21-als.
[24] R. N. Moore and G. S. Fisher, *J. Amer. Chem. Soc.* **78**, 4362 (1956).
[25] W. Battomley, A. R. H. Cole and D. E. White, *J. Chem. Soc.* 2624 (1955).
[26] J. H. Briggs, B. F. Cain and B. R. Davis, *Tetrahedron Letters* No. 17, 9 (1960).
[27] R. Henderson and R. Hodges, *Tetrahedron* **11**, 226 (1960).
[28] E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.* 4073 (1956).
[29] E. A. Chandross and P. Yates, *Chem. & Ind.* 149 (1960).
[30] G. Büchi, R. E. Erickson and N. Wakabayashi, *J. Amer. Chem. Soc.* **83**, 927 (1961).

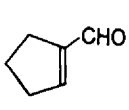
TABLE 1. THE EFFECT OF ω-SUBSTITUENT ON THE ALLYLIC PROTON FREQUENCY OF SOME LONGIFOLENE AND CAMPHENE DERIVATIVES

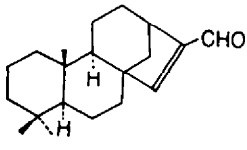
Class	Substituent	Allylic Proton		
		τ(p.p.m.) State	J(cps)	Δτ(p.p.m*)
Longifolene				
	H	7·42 Broad doublet†	3·5	0·0
	CH_2OH	7·05 Broad doublet†	3·5	0·37
	CH_2OAc	7·00 Broad doublet†	3·5	0·42
	CH_2OMe	7·11 Broad hump	—	0·31
	HC=O	6·36 Broad doublet†	4·5	1·06
	CO·OMe	5·95 Broad doublet†	5·0	1·47
Camphene				
	H	7·38 Broad unresolved		0·0
	CH_2OH	7·03 Broad unresolved		0·35
	CH_2OAc	6·98 Broad unresolved		0·40
	HC=O	6·34 Broad unresolved		1·04
	CO·OMe	6·05 Broad unresolved		1·33

* Δτ being the difference: τ value of the parent minus that of the derivative.
† Possibly two unresolved triplets.

derivatives[31] and this has been attributed[24,25] to the higher strain in the bicyclo systems. However, a comparison (Table 2) of the λ_{max} values for ω-formyl-longifolene with that of ω-formylcamphene (XV, X = CHO) revealed that some additional factor must be responsible for this bathochromic shift with respect to camphene system. This red-shift in the longifolene derivatives is general as can be seen from Table 2. This could be attributed to a raised ground state[32,33] rather than a lowered π–π^* transition, in the case of longifolene system. The reason for this higher strain in the ground state of longifolene molecule would appear to be the slight twisting of the

[31] For example cf.





λ_{max}^{EtOH}	237–238 mμ	253, 258 mμ
log ε	4·13	3·87, 3·88

[32] W. M. Schubert and W. A. Sweeney, *J. Amer. Chem. Soc.* **77**, 2297 (1955).
[33] R. L. Erskine and E. S. Waight, *J. Chem. Soc.* 3425 (1960)

TABLE 2. ULTRAVIOLET LIGHT ABSORPTION OF SOME LONGIFOLENE AND CAMPHENE DERIVATIVES

Substituent* X	Camphene†			Longifolene			$\Delta\lambda_{max}$ (mμ)
	λ_{max}^{EtOH} (mμ)		$\varepsilon^{10^{-3}}$	λ_{max}^{EtOH} (mμ)		$\varepsilon^{10^{-3}}$	
CHO	244		17·43	253		15·63	9
COOH	219		14·45	230		11·88	11
COOMe	226		14·36	235		12·43	9
	ε_{210}	ε_{215}	ε_{220}	ε_{210}	ε_{215}	ε_{220}	
H	1255‡	410	251	4455	1932	429	
CH_2OH	4849	1881	896	8660	5712	2580	
CH_2OAc	7207	3913	2781	9040	6328	3390	

* For part structures see Table 1.

† From the data now recorded for camphene systems, it would appear that these do not show any significant bathochromic shift with respect to unbridged cyclopentilidene derivatives e.g. steroidal Δ^{17}-analogues.

‡ cf. O. H. Wheeler and Mateos, *J. Org. Chem.* **21**, 1110 (1956).

C=C bond in longifolene due to the *cis*-fused 7-membered ring. It is well-recognized[34,35] that twisting of an effective double bond in a conjugated system leads to a bathochromic shift. In conformity with the idea of a slight twist in the ethylene linkage of longifolene, the sesquiterpene itself and the ω-hydroxymethyl and ω-acetoxymethyl longifolene showed (Table 2) considerably more intense end-absorption as compared to the corresponding camphene derivatives, indicating, thereby, the expected[36] bathochromic shift for the N → V transition.

EXPERIMENTAL

All m.p. and b.p. are uncorrected. Pet. ether refers to the fraction b.p. 40–60°. All solvent extracts were finally washed with brine, before drying (Na_2SO_4). Rotations were taken in absolute ethanol, unless stated to the contrary. For tetranitromethane (TNM) tests, equal amounts of undiluted compound and 10% solution of the reagent in $CHCl_3$ were mixed.

IR spectra were taken on a Perkin-Elmer Infracord, model 137E, either as smears (liquids) or in nujol (solids); maxima are reported in cm^{-1}. UV spectra were taken on a Perkin-Elmer Spectrophotometer, model 350, in 95% ethanol; the spectra for the longifolene and camphene series were measured under identical conditions. All PMR spectra were taken in a 20% solution in CCl_4 with tetramethylsilane as the internal standard, on a Varian Associates A-60 spectrometer; peaks are reported in τ values.

Longifolene series

ω-Acetoxymethyl longifolene (I)

Longifolene[37] (204 g, 1 mole), paraformaldehyde (36 g, 1·2 mole) and gl. AcOH (400 ml) were refluxed together in an oil bath at 140° for 24 hr (anhydrous conditions). Acetic acid (~330 ml) was, then, distilled off, and the residue cooled, poured into water (350 ml), the oily layer separated

[34] L. L. Ingraham in M. S. Newman's *Steric Effects in Organic Chemistry* pp. 493–495. John Wiley, New York (1956).

[35] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent and G. van Zandt, *Chem. Rev.* **41**, 325 (1947).

[36] R. S. Mulliken and C. C. Roothaan, *Chem. Rev.* **41**, 219 (1947).

[37] Longifolene was obtained as described earlier: U. R. Nayak and Sukh Dev, *Tetrahedron* **8**, 42 (1960).

and the aq. portion extracted with pet. ether (100 ml × 2). The combined organic portions were washed with brine till neutral and dried. After removal of the solvent, the pale yellow liquid residue (272 g) was fractionated (6" Vigreux column) to give after a forerun of longifolene (b.p. 108–110°/2 mm, n_D^{35} 1·5000, α_D +40; 54 g, 27%), ω-acetoxymethyl longifolene, b.p. 154–156°/2 mm, yield 153 g (75% based on unrecovered longifolene); an analytical sample had: b.p. 144°/1 mm, $n_D^{26\cdot5}$ 1·5035, $d_4^{26\cdot5}$ 1·022, M_D 79·93 (Calc. 79·91), $[\alpha]_D$ + 75·2° (neat); TNM test, distinct yellow (Found: C, 78·30; H, 10·11. $C_{15}H_{28}O_2$ requires: C, 78·21; H, 10·21%).

The high boiling residue (59·5 g) in the above fractionation was rectified under high vacuum to yield a fraction b.p. 140–150°/5·5 × 10^{-3}, n_D^{26} 1·4969, yield 13 g; from its elemental analysis, IR absorption and PMR spectrum it is undoubtedly a diacetate, expected as a by-product in the Prins condensation.

Homolongifolane (II) *and ω-acetoxymethyl longifolane*

The above acetate (6·875 g) in acetic acid (20 ml) over prereduced Adam's Pt catalyst (200 mg) consumed 1224 ml (1·79 mole) H_2 during 4 hr at 28°/686 mm, when further absorption of H_2 ceased. The usual work up gave a product (6·55 g) which was carefully fractionated. The first fraction after redistillation over sodium proved to be the saturated hydrocarbon, homolongifolane (3·8 g, 69%): colourless mobile liquid, b.p. 112–113°/3 mm, n_D^{26} 1·4952, d_4^{26} 0·9260, M_D 69·30 (Calc: 69·52), $[\alpha]_D$ −36° (*c*, 4·85%); TNM test, negative. (Found: C, 87·34; H, 12·62. $C_{16}H_{28}$ requires: C, 87·19; H, 12·81%).

The second fraction was refractionated to furnish the saturated acetate (1·55 g, 23%) as a colourless liquid, b.p. 150–155°/3 mm, TNM test, negative (Found: C, 78·09; H, 10·88. $C_{18}H_{30}O_2$ requires: C, 77·65; H, 10·86%).

ω-Hydroxymethyl longifolene (III)

The Prins acetate (82·8 g, 0·3 mole) was mixed with a solution of KOH (33·6 g) in water (30 ml) and ethanol (300 ml) with cooling and left aside at room temp (28°) for 18 hr. The reaction mixture was diluted with ice-water (300 ml) extracted with pet. ether (100 ml × 3), washed neutral and dried; solvent removal yielded the alcohol as a crystalline solid, m.p. 60–62° softening at 54°), yield quantitative. The product after two recrystallizations from pet. ether at 0° gave colourless needles, m.p. 68–69°, $[\alpha]_D$ +63·3° (*c*, 1·98%) in a yield of over 60%; TNM test, clear yellow; IR spectrum: OH 3200, 990; C=C 1670. (Found: C, 82·01; H, 11·37. $C_{16}H_{26}O$ requires: C, 81·99; H, 11·18%). The material is best stored in a polythene bottle at 0°.

The 3,5-*dinitrobenzoate* was prepared from the alcohol (0·5 g), the acid chloride (0·6 g), dry benzene (10 ml) and dry pyridine (1 ml) at 50° for 2·5 hr. The crude product (1 g, m.p. 119–122°) was recrystallized from benzene–pet. ether to give colourless crystals, m.p. 133–134°, $[\alpha]_D$ +74·1° (*c*, 1·6% in $CHCl_3$). (Found: N, 6·54. $C_{23}H_{28}O_6N_2$ requires: N, 6·54%).

ω-Methoxymethyl longifolene (VII)

The acetate (5·5 g, 0·02 mole), absolute methanol (50 ml) and sulphosalicylic acid (300 mg) were refluxed in a flask fitted with a fractionation column having a total condensation partial take-off type still head; the methyl acetate formed was tapped off every 0·5 hr together with some methanol during the first few hrs in a total time of 23 hr. The reaction mixture was poured into water (100 ml), extracted with pet. ether (20 ml × 3), washed neutral and dried. The solvent was flashed off and the residue distilled yielding ω-methoxymethyl longifolene (4·1 g, 82%) as a colourless liquid, b.p. 147–148°/4 mm, n_D^{29} 1·5035; IR spectrum: OCH_3 1110; C=C 1660. (Found: C, 82·24; H, 11·05. $C_{17}H_{28}O$ requires: C, 82·20; H, 11·36%).

The above ether on exposure to air during several days deposited some solid. The air-oxidized sample (test for peroxides, positive) was taken up in ether and separated into acidic and neutral parts by extraction with aq. Na_2CO_3. The crude acid (m.p. 180–193°) after recrystallization from aq. acetic acid yielded colourless needles m.p. 205–206°, identified as ω-carboxy-longifolene, described below.

ω-Formyl longifolene (IV)

(i) *Oxidation with active* MnO_2. The optimum conditions, described below, for this oxidation were first established by following the course of oxidation in pilot experiments, spectrophotometrically.

A mixture of the unsaturated alcohol (10 g), dry n-hexane (400 ml) and active MnO_2[38] (60 g) was vigorously stirred (N_2) for 48 hr. Peroxide-free ether (300 ml) was then added and after stirring for another 30 min, the reagent was filtered off, the solid washed with ether and the combined filtrates freed from the solvent under suction in a feeble current of N_2. The crude product (9·0 g; ε_{253} 9000) slowly crystallized out in a refrigerator; the waxy product, m.p. 58–61°, after two crystallizations (N_2 atm) from pet. ether at −10° gave colourless crystals m.p. 65–67°, $[\alpha]_D$ +169·9° (*c*, 6·26%); TNM test, very faint pale yellow. (Found: C, 81·63; H, 10·43. $C_{16}H_{24}O$ requires: C, 82·70; H, 10·41%). A better elemental analysis could not be obtained due to its great susceptibility to air oxidation.

(ii) *Oxidation with chromic acid.* The alcohol (93·6 g, 0·4 mole) dissolved in acetone (distilled over $KMnO_4$; 200 ml) and n-hexane (320 ml) was cooled to −10° and treated slowly, under vigorous stirring, with a cold solution of CrO_3 (40 g, 0·4 mole) in water (100 ml) containing H_2SO_4 (conc, 34·4 ml), at such a rate that the reaction temp did not exceed 15° (1–1/2 hr). Stirring was continued for another 3 hr at ~0°, when the hexane layer was separated, the aq. phase diluted with water and extracted with pet. ether (100 × 1). The combined organic phases were washed with water (100 ml × 1) and then with 5% aq. NaOH (if proper temp control during oxidation had not been maintained, these aq. alkaline washings on acidification will yield ω-carboxy longifolene), washed neutral and dried. Removal of the solvent yielded the crude aldehyde (78·6 g; ε_{253} 11,200), which slowly solidified at 0°, m.p. ~65°.

The *semicarbazone* (pyridine method) after two crystallizations from alcohol–pyridine was obtained in clusters of colourless needles, m.p. 238°, λ_{max} 279 mμ (ε = 35,480). Found: C, 70·86; H, 9·26; N, 14·62. $C_{17}H_{27}ON_3$ requires: C, 70·55; H, 9·40; N, 14·52%).

The 2,4-*dinitrophenylhydrazone*, prepared *via* the semi-carbazone was first crystallized from alcohol–pyridine and then from benzene–pet. ether (1:1) to furnish red microprisms, m.p. 219–220°, λ_{max}^{chf} 390 mμ (ε 31,620). (Found: 63·39; H, 7·02; N, 13·57. $C_{22}H_{26}O_4N_4$ requires: C, 64·06; H, 6·84; N, 13·58%).

ω-Carboxy longifolene (V)

(i) *By silver oxide oxidation.* To a rapidly stirred mixture of crude aldehyde (4·6 g) and aq. $AgNO_3$ (10·2 g in 20 ml water), a solution of NaOH (7·2 g) in water (70 ml) was added rapidly (2 min). The reaction mixture was stirred and heated on a water bath (85°) for 75 min. The black ppt was filtered, washed with hot water and the brown filterate charcoaled. The clarified solution was acidified (HCl) and the precipitated acid collected after several hr, yield 4·0 g, m.p. ~190°. The product was recrystallized from aq. acetic acid to furnish white micro needles (2·5 g), m.p. 206–207° (Naffa and Ourisson[7] report m.p. 205–206°), $[\alpha]_D$ +103·2° (*c*, 1·26%); IR spectrum: COOH 2300–2650, 1675, 1575(?), 1225. (Found: C, 77·18; H, 9·68. $C_{16}H_{24}O_2$ requires: C, 77·37; H, 9·74%).

(ii) *By air oxidation.* To a solution of the crude aldehyde (21·2 g) in acetic acid (100 ml), manganese acetate (2 g) dissolved in acetic acid (20 ml) was added, and the mixture heated to 75–80° while passing a fairly rapid and well-dispersed current of dry air. More solvent had to be added occasionally to make good the loss. After a total reaction period of 48 hr, the reaction mixture was diluted with water and extracted with ether (50 ml × 3). The extract was separated into alkali-soluble and neutral portions by extraction with 5% aq. NaOH. The alkaline solution on acidification yielded the required acid as a pale yellow solid, m.p. 195–200°, yield 11·2 g, which after recrystallization from aq. acetic acid had m.p. 206–207°.

ω-Carbomethoxy longifolene

The acid (5 g), absolute methanol (10 ml), dry benzene (15 ml) and conc H_2SO_4 (1·5 ml) were refluxed (water-bath) for 8 hr and worked up in the usual manner to give the methyl ester as a colourless liquid (4·9 g), b.p. 142–143°/1 mm, $n_D^{28.5}$ 1·5171, $[\alpha]_D$ +104·1° (neat); TNM test, faint pale yellow; IR spectrum: COOMe 1720, 1200, 1180, 1160, 1132; C=C 1655. (Found: C, 77·30; H, 9·96. $C_{17}H_{26}O_2$: requires: C, 77·82; H, 9·99%).

[38] O. Mancera, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.* 2189 (1953).

Camphene Series

Acetoxymethylation of camphene

Camphene[39] (25 g, 0·18 mole), p-formaldehyde (6·8 g) and gl. AcOH (625 ml) were reacted and worked up exactly as described for longifolene. The crude product (26 g) was fractionated and the fraction b.p. 100–118°/8 mm (20 g) collected separately. Gas-liquid chromatography (GLC)[40] showed this to contain ~84% of the required acetate. Since the material and products derived from this were required for a spectroscopic study it was decided to prepare these samples from a crystalline member of this series. In pilot experiments it was found that ω-carboxy-camphene, readily obtainable from the Prin's product, would be suitable for this purpose.

ω-Carboxy camphene

The above product (10 g) was mixed with a solution of KOH (5·6 g) in water (6 ml) and ethanol (50 ml) and left aside at room temp (25–29°) for 22 hr. The product was worked up, as described for ω-hydroxymethyllongifolene, to yield a pale yellow liquid (8·3 g) which was distilled, b.p. 94–102°/1·7 mm, to give 7·48 g of a colourless liquid. This was taken up in acetone (30 ml) and n-hexane (50 ml) and chilled in an ice-salt bath. A cold solution of CrO_3 (4·5 g) in conc H_2SO_4 (4 ml) and water (10 ml) was added dropwise with vigorous stirring during 30 min, maintaining the temp between −10 to 0°. The reaction mixture was further stirred at this temp for 2–1/2 hr, when the solvent layer was removed and the aq. part extracted with hexane (50 ml × 3). The combined extracts were washed with aq. Na_2CO_3 (10%; 100 ml × 3) and dried. Removal of solvent furnished the aldehyde as a yellow liquid (5·9 g).

The above aldehyde (5·8 g), $AgNO_3$ (12·5 g) in water (25 ml), and NaOH (9 g) in water (88 ml) were mixed and stirred on a steam-bath for 1½ hr. The reaction mixture was worked up, as described for ω-carboxy longifolene, to yield a solid (3·9 g), m.p. 121–123°. Recrystallization from aq. ethanol gave white glistening flakes m.p. 123–124°, yield 2·1 g, IR spectrum: COOH 2300–2700, 1690, 1650. (Found: C, 72·84; H, 8·71. $C_{11}H_{16}O_2$ requires: C, 73·30; H, 8·95%).

The *methyl ester* was prepared by the action of diazomethane in ether solution. The product had: b.p. 94°/4 mm, $n_D^{28.5}$ 1·4972. IR spectrum: COOMe 1733, 1200, 1180, 1160, 1145; C=C 1653. (Found: C, 73·99; H, 8·98. $C_{12}H_{18}O_2$ requires: C, 74·19; H, 9·34%).

ω-Hydroxymethyl camphene

To a well-dispersed suspension of $LiAlH_4$ (0·9 g, 0·024 mole) in dry ether (50 ml) a solution of the acid (2·08 g, 0·012 mole) in dry ether (30 ml) was introduced (5 min) with stirring and cooling in an ice-salt bath. The reaction mixture was stirred in the same bath for another 1–1/2 hr and then left aside at room temp (25–29°) for 17 hr. The product was chilled in a freezing mixture, treated cautiously with water (20 ml) and then with 100 ml of 20% aq. Rochelle salt solution. Usual work up gave the desired alcohol as a colourless liquid (single peak in GLC) b.p. 87–88°/1·5 mm, yield 1·7 g. IR spectrum: OH 3300, 990; C=C 1670. (Found: C, $\frac{78·89}{79·38}$; H, $\frac{10·94}{10·96}$. $C_{11}H_{18}O$ requires: C, 79·46 H, 10·92%).

ω-Acetoxymethyl camphene

The above alcohol (0·21 g) was acetylated with Ac_2O (2 g) and pyridine (2 ml) at room temp (25–29°) during 19 hr and then worked up to yield the acetate (single peak in GLC) as a colourless liquid, b.p. 88°/1·7 mm. yield 0·21 g. IR spectrum: OAc: 1745, 1230; C=C 1670 (Found: C, 74·98; H, 9·43. $C_{13}H_{20}O_2$ requires: C, 74·96; H, 9·68%).

ω-Formyl camphene

ω-Hydroxymethyl camphene (0·116 g) in hexane (10 ml) was shaken with active MnO_2 (2·0 g) for 11 hr at room temp (28–29°). On working up in the usual manner, the aldehyde was obtained

[39] A commercial product (B.D.H. m.p. ~45°) was repeatedly crystallized from alcohol to yield a gas chromatographically homogeneous material, m.p. 48–48·5°, $[\alpha]_D$ +19·9° (*c*, 0·5%).

[40] All GLC, reported herein, were carried out at 160° (column temp.) over an ethylene glycol succinate (20%)/Chromosorb W column (2 meters) using H_2 as the carrier gas.

as a colourless liquid (single peak in GLC) at 1·4 mm from a bath at 120° yield 31 mg. IR spectrum: CHO 2703, 1670; C=C 1626. (Found: C, 79·96; H, 9·61. $C_{11}H_{16}O$ requires: C, 80·44; H, 9·83%).

The *semicarbazone* (pyridine method) crystallized from pyridine–ethanol as white micro needles, m.p. 219–220°. (Found: C, 65·54; H, 8·13; N, 18·54. $C_{12}H_{19}N_3O$ requires: C, 65·12; H, 8·65; N, 18·99%).

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