for aromatic male pheromones in other noctuid species[18]. The fact that an average 16 µg of 2-phenylethanol was isolated from each male moth is a strong indication that the pheromone is stored in the body of *T. ni* in uncombined form. In *M. configurata*, it is stored as the hexoside and released in pure form, as needed, by enzymic hydrolysis.

In recordings from single olfactory receptors of the antenna of female *T. ni* conducted by one of us (E.P.), certain cells innervating sensory hairs (Sensilla trichodea) specifically responded to both 2-phenylethanol and male scent brush extract. Within the same type of sensillum, other receptor cells responded maximally to the corresponding aldehyde, phenylacetaldehyde. This compond has long been known[23,24] as a strong distance attractant for the female (and to a lesser degree, the male) cabbage looper, and was initially considered by us as the prime candidate structure for the male pheromone. However, no trace of phenylacetaldehyde could be detected in the scent brush extract, and in our behavioural bioassay this compound was totally inactive at all doses. Detailed reports will be given elsewhere on the responses of single pheromone receptor cells of the female *T. ni*, and on the chemical specificity of 2-phenylethanol determined by the novel laboratory behavioural bioassay described here.

HENDRICKS and SHAVER[25] have recently shown that an unidentified pheromone released from the hairpencils of another noctuid, the male *Heliothis virescens* (F.), prior to mating, suppresses the emission of sex pheromone by the female insect. Should this be true of 2-phenylethanol for *T. ni*, it might conceivably be used in controlling this pest through mating suppression. This interesting possibility is presently under investigation[26].

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[26] We thank Dr. P. A. GIANG for infrared spectra, Dr. N. WAKABAYASHI for gas chromatograms, Dr. R. M. WATERS for NMR-spectra, Dr. S. DUTKY for mass spectra, and Miss D. GOUGH for technical assistance in rearing the insects.

Jungermanool, a New Labdane Diol from the Liverwort, *Jungermannia torticalyx* Steph.[1]

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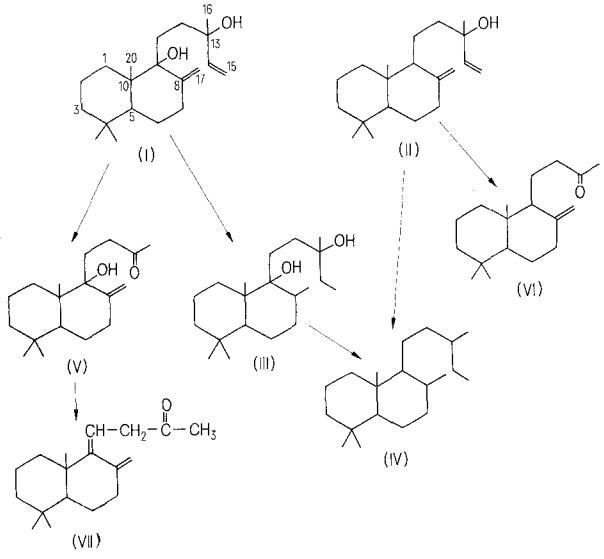
Summary. A new diterpenoid named jungermanool was isolated from *Jungermannia torticalyx* and the structure was found to be labda-8 (17), 14-dien-9, 13-diol by chemical and spectroscopical methods.

From the liverwort, *Jungermannia torticalyx* Steph., we isolated a new diterpene diol (I) named jungermanool together with (–)-manool[3], whose structure was determined to be represented by formula I.



Jungermanool (I), $C_{20}H_{34}O_2$ (M$^+$ 306); mp 124–125°; $[\alpha]_D$ –49.3°, was isolated from a hexane extract of the plant by elution chromatography. The IR- and PMR-spectra[4] resembled closely those of manool in the whole pattern. They exhibited the presence of 4 tertiary methyls (ν 1390, 1380, 1370 cm^{-1}; δ 0.81, 0.90, 1.00, 1.21, each 3H, s), 1 vinyl and 1 exomethylene (ν 3090, 1640, 987, 917, 880 cm^{-1}; δ 4.97, 1H, d.d, J=10.0, J=2.5; δ 5.15, 1H, d.d, J=15.0, J=2.5; δ 5.90, 1H, d.d, J=15.0, J=10.0; δ 4.52, 4.79, each 1H, br.s) as well as 2 tertiary hydroxyl groups (ν 3640, 3610, 3470 cm^{-1}). Its saturated tetrahydro derivative (III), $C_{20}H_{38}O_2$ (M$^+$ 310); mp 69–70°; $[\alpha]_D$ –26.9°; ν 3630, 3610, 3450 cm^{-1}, which was obtained by catalytic hydrogenation of the diol over PtO_2 in AcOH, after being dehydrated with $SOCl_2$ in pyridine, was submitted to catalytic hydrogenation over PtO_2 in AcOH to give labdane (IV),[5] $C_{20}H_{38}$ (M$^+$ 278); $[\alpha]_D$ –6.7°, which was identified by the coincidence of the IR-, PMR- and MS-spectra with those of an authentic sample prepared from manool. In addition, when the diol (I) was oxidized with $KMnO_4$ in acetone, a bisnor compound (V), $C_{18}H_{30}O_2$ (M$^+$ 278); mp 64–65°; $[\alpha]_D$ –55.0°;

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[2] The authors wish to express their gratitude to Dr. T. SEKI, Department of Botany, Hiroshima University, for the collection and identification of the liverwort.

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The CMR characteristics of jungermanool

Carbon	Chemical shift	Multiplicity
1	31.9[a]	t
2	18.8	t
3	32.7[a]	t
4	38.6	s
5	48.6	d
6	27.5	t
7	36.2	t
8	148.2	s
9	77.3	s
10	43.6	s
11	28.9	t
12	41.2	t
13	73.4	s
14	145.4	d
15	111.4	t
16	28.0	q
17	106.5	t
18	24.4	q
19	17.8	q
20	17.8	q

[a] May be interchanged.

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ν 3640, 3550, 1715 cm^{-1}; δ 0.87, 0.93, 1.01, 2.02, each 3H, s; δ 4.43, 4.78, each 1H, s, due to loss of the vinyl group was obtained as well as in the case of manool (II→VI)[6]. However, compound V was characterized as a keto-alcohol with a tertiary hydroxyl group, while the oxidation product from manool was a ketone (VI), $C_{18}H_{30}O$ (M^+ 262); $[\alpha_D]$ −31.4°; ν 1715 cm^{-1}. These facts revealed jungermanool as a derivative of manool with an additional tertiary hydroxyl group. To determine the position of the remaining hydroxyl group, the keto-alcohol was further treated with $SOCl_2$ in pyridine to give a diene (VII), $C_{18}H_{28}O$ (M^+ 260); $[\alpha]_D$ +41.3°; ν 1715, 1644, 880 cm^{-1}; δ 0.90, 1.06, 1.06, 2,03, each 3H, s; δ 2.72, 2H, d, J=3.8; δ 4.55, 4.88, each 1H, br.s; δ 5.41, 1H, t, J= 3.8, which showed a UV-absorption band, $\lambda_{max}^{isooct.}$ 213 nm (ε 7150), attributable to a conjugated diene system, bisexocyclic to a cyclohexane ring[7]. The formation of this conjugated diene system is reasonably explained by locating the additional tertiary hydroxyl group on C-9 of the labdane carbon skeleton. The gross structure of jungermanool is thus determined to be labda-8 (17), 14-dien-9, 13-diol (I).

This structure was supported by the fact that in measuring PMR-spectra of jungermanool and manool with application of the shift reagent, Eu(dpm)$_3$, the exomethylene protons of jungermanool, which are close to the C-9 hydroxyl group in the proposed structure, showed the most remarkable variation between the signal shifts of the corresponding protons of both alcohols. A further support was also obtained by the single frequency offset resonance ^{13}C-NMR-spectrum (Table)[8,9] which consists of 5 singlets (1 olefinic carbon: 148.2; 2 carbinyl carbons: 73.4, 77.3; 2 fully substituted carbons: 38.6, 43.6); 2 doublets (1 olefinic: 145.4, 1 methine carbon: 48.6); 9 triplets (2 olefinic: 106.5, 111.4; 7 usual methylenes: 18.8, 27.5, 28.9, 31.9, 32.7, 36.2, 41.2) and 4 methyl quartets (17.8, 17.8, 24.4, 28.0).

Synthetic Simulation of Nonribosomal Peptide Biosynthesis. A Dual Role of Alkylthiol Esters in Peptide Synthesis

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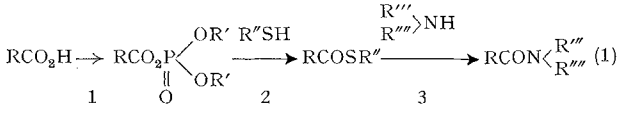
Summary. Coupling of peptide alkylthiol esters with amino acid derivatives in the presence of pivalic acid or 2-hydroxypyridine proceeds without racemization. A dual role of alkylthiol esters as protective and reactive functions in peptide synthesis was well proved.

Recent studies on nonribosomal peptide biosynthesis[1], represented by gramicidin S and tyrocidine biosynthesis, have revealed that α-amino acids are activated with ATP to give mixed anhydrides (step 1) which are transformed into alkylthiol esters (step 2), followed by the peptide bond formation (step 3):



(1)

We have already reported[2] a general method for preparing thiol esters from carboxylic acids and thiols using diethyl phosphorocyanidate[3] ($NCPO(OEt)_2$, DEPC) or diphenyl phosphorazidate[4] ($N_3PO(OPh)_2$, DPPA) in combination with triethylamine[5]. This thiol ester formation reaction will be regarded as steps 1 and 2 in equation 1 because the intermediates will possibly be mixed phosphoric carboxylic anhydrides[4]. We now wish to report realization of the laboratory analogy for step 3

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