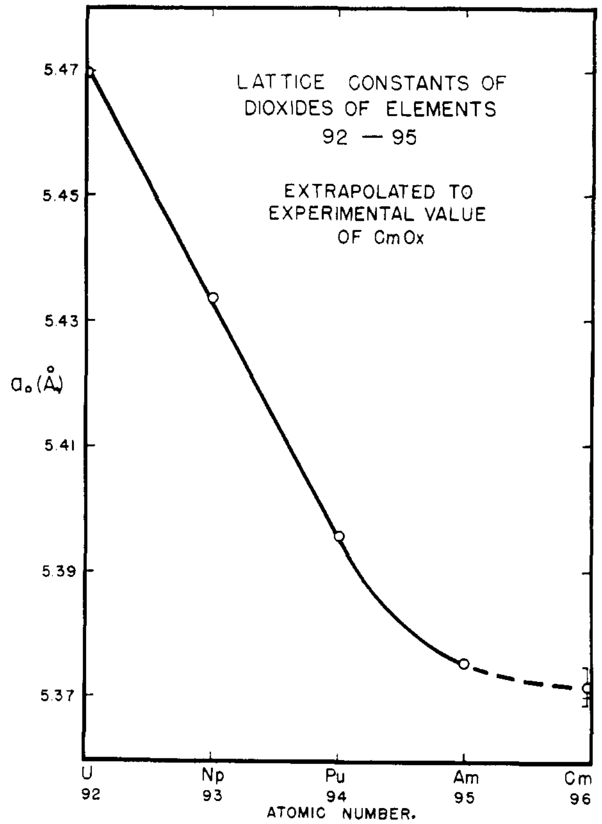

Fig. 1.

lattice constants. A reasonable extrapolation of the smooth curve would give $\sim$5.37 for the expected value of CmO$_2$. Our value of 5.372 would indicate that the ratio of O/Cm must be close to 2, showing the existence of an "average valence" of Cm approaching 4.

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## CRYSTALLINE HIGH POLYMERS OF $\alpha$-OLEFINS

*Sir:*

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained[1] by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

Using various heterogeneous solid catalysts which will be described elsewhere,[2] we have synthesized linear crystalline polymers of $\alpha$-olefins and we are now reporting some properties of crystalline polypropylene, poly-$\alpha$-butylene, and polystyrene. Depending on the structure of the catalyst, different amounts (ranging from 0 to 100%) of the polymerization products are crystallizable and can be separated easily from the much more soluble non-crystalline polymers by solvent extraction. In the case of polypropylene and polystyrene the X-ray diagrams of drawn fibers show reflections from about fifty different planes. Both equatorial and higher order X-ray reflections of polystyrene may be indexed on the basis of a hexagonal cell with $a$ = 21.9 Å., and $c$ = 6.65 Å. (space-group R 3c or R $\bar{3}$c). One of the two different crystal forms we observed for the poly-$\alpha$-butylene seems to have a similar cell with $a$ = 17.3 Å. and $c$ = 6.7 Å. We have not yet collected sufficient data to establish the correct unit cell of polypropylene: the identity period along the fiber axis $c$ is, in this case, 6.50 Å.; the equatorial X-ray reflections may be indexed on the basis of an oblique cell with $a$ = 6.56 Å., $b$ = 5.46 Å. and $\gamma$ = 106° 30′.

In Table I the physical properties of the crystalline polypropylene and poly-$\alpha$-butylene have been compared with those of the corresponding solid non-crystallizable substantially linear polymers obtained as by-products by the same polymerization processes.

The new crystalline polyhydrocarbons show higher melting point, higher density and lower solubility in organic solvents, than the corresponding "amorphous" polyhydrocarbons having intrinsic viscosity of the same order of magnitude.

The infrared spectra[3] of crystalline polypropylene, of melted samples of the same polymer and of the "amorphous" polypropylene show between 2 and 7.5 $\mu$ the high adsorption regions characteristic of hydrocarbons. The wave lengths of the absorption bands between 7.5 and 15 $\mu$ in normal and polarized light have been reported in the Table II. Most of the differences between the infrared spectrum of the crystalline and of the non-crystalline polypropylene[4] disappear on melting the crystalline product and reappear after cooling the melted sample.

The large number and the cleanness of the X-ray reflections obtained from drawn fibers of the new polyhydrocarbons demonstrate the unusual regularity of their chain structure. By comparing X-ray and density data are seen that each stretch of principal chain, included in the elementary cell, corresponds to three monomeric units (–CH$_2$–CHR– and therefore contains an odd number of asymmetric carbon atoms.

For these reasons we have excluded the presence of sequences of asymmetric carbon atoms having alternatively $d$ and $l$ configuration in the principal chain of the polymer, as was proposed for the crystalline poly-alkylvinyl ethers.[5]

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[1] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 56.

[2] Details on the polymerization processes will be published in the *Journal of Polymer Science* and *Atti dell'Accademia Nazionale dei Lincei*.

[3] A Beckmann IR 2, a Perkin-Elmer model 112, and a Perkin-Elmer model 21 spectrometer with NaCl prisms have been used.

[4] The infrared spectra of the crystalline and of the linear not crystallizable polypropylene are very different from infrared spectra of branched polypropylene produced using AlBr$_3$ as catalyst.

[5] C. E. Schildknecht, *et al.*, *Ind. Eng. Chem.*, **40**, 2104 (1948); C. E. Schildknecht, S. T. Gross and A. O. Zoss, *ibid.*, **41**, 1998 (1949); C. E. Schildknecht, A. O. Zoss and F. Grosser, *ibid.*, **41**, 2391 (1949).

TABLE I

PHYSICAL PROPERTIES OF "CRYSTALLINE" AND "AMORPHOUS" (NOT CRYSTALLIZABLE) POLYPROPYLENE, POLY-$\alpha$-BUTYLENE AND POLYSTYRENE

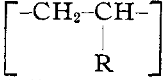
| | Intrinsic viscosity[a] cm.$^3$/g. × 10$^2$ | Identity period along the chain, Å. | X-Ray density, g./cm.$^3$ | Density $d^{25}_{25}$ | X-Ray[d] or dilatometric[e] transition point, °C. | Melting point, ° C. | Solubility[f] Ether | Solubility[f] $n$-Heptane | Solubility[f] Toluene |
|---|---|---|---|---|---|---|---|---|---|
| Polypropylene | | | | | | | | | |
| (a) h.m.w. "crystalline" | 2.40[b] | 6.50 ± 0.05 | 0.94 | 0.92 | 158–160[d] | .. | i. | i. | s. |
| (b) l.m.w. "crystalline" | 0.17[b] | (6.50 ± 0.05) | 0.94 | 0.91 | 148–150[d] | .. | i. | sl.s. | s. |
| (c) "amorphous" | 0.55[b] | ... | ... | 0.85 | ... | 75 | s. | s. | v.s. |
| Poly-$\alpha$-butylene | | | | | | | | | |
| (a) "crystalline" | 1.02[b] | 6.7 ± 0.1 | 0.96 | 0.91 | 126–128[d] | .. | i. | s. | v.s. |
| (b) "amorphous" | 0.35[b] | ... | ... | 0.87 | ... | 65 | s. | v.s. | v.s. |
| Polystyrene | | | | | | | | | |
| (a) "crystalline" | 3.8[c] | 6.65 ± 0.05 | 1.12 | 1.08 | 230[d,e] | .. | i. | i. | v.s. |

[a] Concentrations at 25°. [b] Tetralin as solvent at 135°. [c] Benzene as solvent at 25°. [d] Temperature at which all the X-ray reflections of crystals disappear. [e] First order transition point from dilatometric data. [f] i. = insoluble; sl.s. = slightly soluble; s. = soluble; v.s. = very soluble.

TABLE II

INFRARED SPECTRUM OF DIFFERENT TYPES OF POLYPROPYLENE BETWEEN 7.5 AND 15 $\mu$

| Crystallizable polypropylene | | | | |
|---|---|---|---|---|
| | Crystalline cold drawn product ↕ E-vector | | | |
| Crystalline product | ↕ | ↔ | Melted product | Amorphous not crystalliz. polypropylene |
| 7.53 w | ... | 7.53 w | ... | ... |
| 7.67 m | 7.67 m | ... | ... | 7.67 w |
| 7.71 sh | ... | 7.72 w | ... | ... |
| 7.97 m | 7.96 m | ... | 7.97 w | 7.97 m |
| ... | ... | ... | ... | 8.13 m |
| 8.20 | ... | 8.20 w | ... | ... |
| 8.57 s | 8.56 s | sh | ... | ... |
| 8.66 sh | sh | 8.67 m | 8.70 s,b | 8.66 s |
| 9.06 w | 9.06 w | 9.06 w | 9.06 w | 9.06 sh |
| 9.57 w | 9.57 w | ... | ... | ... |
| 9.65 sh | ... | ... | ... | ... |
| 10.02 s | 10.02 s | 10.02 w | 10.02 w-m | 10.02 w-m |
| 10.28 s | 10.28 s | 10.28 m | 10.28 s | 10.28 s |
| 10.64 w | ... | 10.63 w | ... | ... |
| 11.12 m | 11.12 vw | 11.12 m | Wide absorption region between 11 $\mu$ and 12.7 $\mu$ with absorption maxima at 12.38 and 11.2 $\mu$ | Wide absorption region between 11 $\mu$ and 12.7 $\mu$ with absorption maxima at 12.3 $\mu$ and 11.90 $\mu$ and shoulder at 11.21 $\mu$ |
| 11.89 s | 11.89 s | 11.89 w | | |
| 12.36 m | 12.36 vw | 12.36 m | | |

Since the sequences of the type *d-l-l* or *l-d-d* do not seem probable, we attribute to the new crystalline polymers a structure in which at least for long portions of the principal chain, all the asymmetric carbon atoms have the same configuration.[6] In this case, if the principal chain of a crystalline polymer of an $\alpha$-olefin  $\left[-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-\right]$, is represented arbitrarily as a planar fully extended chain, all the R groups must be placed on the same side of the plane of the principal chain. Such planar structure is impossible because of the steric impediments among the R groups and in order to reach the crystalline state a spiralization of the principal chains must take place.

This hypothesis agrees with the value found for the identity period (6.5–6.7 Å) of all these polymers, which is shorter than the length of a planar and fully extended paraffinic chain corresponding to three monomeric units (7.62 Å.).

We suppose that a similar structure may be attributed to the crystalline polyalkylvinyl ethers having identity periods along the principal chain[7] roughly as long as those observed in the crystalline polyhydrocarbons we have prepared, and

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(6) We propose to designate as "isotactical chains," from the Greek words ἴσος = and τάττω = to set up, the polymer chains having such exceptionally regular structure, containing series of asymmetric carbon atoms with the same steric configuration ("isotactical" asymmetric carbon atoms).

(7) C. E. Schildknecht, S. T. Gross, H. R. Davidson, I. M. Lambert and A. O. Zoss, *Ind. Eng. Chem.*, **40**, 2104 (1948).

different properties from ordinary soft polymers.[8]

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RECEIVED DECEMBER 10, 1954

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[8] S. H. Muthana and H. Mark, *J. Polymer Sci.*, **4**, 531 (1949).

[9] X-Ray structure determinations.

[10] Viscosity and density determinations.

[11] Infrared spectra determinations.

[12] Polymerization of α-olefins.

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## THE ISOLATION OF α-PELTATIN GLUCOSIDE FROM THE RHIZOMES OF *PODOPHYLLUM PELTATUM L.*

*Sir:*

The antimitotic substances obtained from the American species of Podophyllum (*P. peltatum L.*) are present in the form of sugar-free compounds isoluble in water as well as in the form of fairly readily soluble derivatives of these compounds with glucose. The aglucones, which are soluble in chloroform, can be isolated from the crude drug together with the resins: from this fraction, three different substances could be crystallized, *viz.*, podophyllotoxin, which is also found in *Indian P. emode* Wall., and in species of Juniperus,[1] and α- and β-peltatin,[2] which are characteristic of American Podophyllum.

The glucosides hitherto isolated from *P. peltatum* are derivatives of podophyllotoxin and β-peltatin.[3] Each of these two natural products is a white amorphous powder which, on treatment with β-glucosidase, easily splits into the crystalline aglucone and 1 mole D-glucose. We have now succeeded in isolating a further uniform glucoside from the more water-soluble fractions obtained by partition chromatography between different solvents during the isolation of the other two glucosides. In comparison with the previously known amorphous Podophyllum glucosides, the new glucoside readily crystallizes, a fact that facilitates its isolation.

The new glucoside crystallizes from acetone in colorless, long prisms which melt, with decomposition, at 168–171°. The specific rotation is $[\alpha]^{20}\mathrm{D}$ −128.9° (*c* 0.5 in methanol). Analysis confirmed the formula $C_{27}H_{30}O_{13}$ (calcd. C, 57.65; H, 5.38; O, 36.98; $OCH_3$, 11.03. Found: 57.77; H, 5.50; O, 37.08; $OCH_3$, 10.93). The ultraviolet absorption spectrum exhibits a maximum at 280 mμ (log ε 3.51). The glucoside is readily soluble in alcohol and fairly readily soluble in water. The reaction with ferric chloride is positive: the color being rust-red in water and green in alcohol. These positive color reactions indicate the presence of a free phenolic hydroxyl group; thus, the new glucoside differs distinctly from the two hitherto known amorphous glucosides of *P. peltatum* which do not show any color reaction with ferric chloride.

On acetylation with acetic acid anhydride in pyridine, the penta-acetyl derivative, which crystallizes from methanol in bunches of thin, white prisms, can be obtained. It melts at 222–223° and has an optical rotation $[\alpha]^{20}\mathrm{D}$ −96.0° (*c* 0.5 in chloroform). Analysis led to the formula $C_{37}H_{40}O_{18}$ (calcd. C, 57.51; H, 5.22; O, 37.27; $OCH_3$, 8.03; 5 $COCH_3$, 27.85. Found: C, 57.30; H, 5.46; O, 37.04; $OCH_3$, 7.98; 5 $COCH_3$, 27.60). This derivative is practically insoluble in water, and the ferric chloride reaction is negative.

The new glucoside is easily hydrolyzed by β-glucosidase at *p*H 5 into aglucone and sugar. The aglucone can be readily obtained in pure crystalline form because of the uniformity of the starting material, and it has been found to be identical with α-peltatin (Ib). The compound, which crystallizes from absolute alcohol in flat prisms, melts at 242–246°[4]; the optical rotation is $[\alpha]^{20}\mathrm{D}$ −124.5° (*c* 0.5 in chloroform).[4] The mixed melting point with an authentic sample,[5] further purified by chromatography, showed no depression. The analysis confirmed the formula $C_{21}H_{20}O_8$ (calcd. C, 63.00; H, 5.04; O, 31.97; $OCH_3$, 15.50. Found: C, 62.98; H, 5.06; O, 31.81; $OCH_3$, 15.69). In the ultraviolet absorption spectrum there is a maximum at 274 mμ (log ε 3.40) which is in good agreement with the value given for α-peltatin in the literature.[4]

For further characterization, the aglucone was acetylated; this resulted in an acetyl derivative, which crystallizes in prisms from absolute alcohol. The melting point was 233–234°, the optical rotation was $[\alpha]^{20}\mathrm{D}$ −113.2° (*c* 0.5 in chloroform). Analysis confirmed the presence of a diacetate and therefore the formula $C_{25}H_{24}O_{10}$ (calcd. C, 61.98; H, 4.99; O, 33.03; $OCH_3$, 12.81; $COCH_3$, 17.77. Found: C, 62.10; H, 5.12; O, 32.84; $OCH_3$, 12.86; $COCH_3$, 1758).

The sugar obtained on enzymatic cleavage could be identified as D-glucose in the form of α-methyl-D-glucoside<1.5>.

As α-peltatin contains two free phenolic hydroxyl groups, one in ring A and one in ring C, it was still uncertain as to which hydroxyl group the sugar residue was attached to. Methylation, by means of diazomethane of the hydroxyl group in the glucoside, produced an amorphous product which melted at 154–156° and showed an optical rotation $[\alpha]^{20}\mathrm{D}$ −122.4° (*c* 0.5 in methanol) and $[\alpha]^{20}\mathrm{D}$ −169.4° (*c* 0.5 in pyridine). The analysis of a sample dried in a desiccator confirmed the formula $C_{28}H_{32}O_{13} \cdot 1\ H_2O$ (calcd. C, 56.56; H, 5.76; $OCH_3$, 15.66. Found: C, 56.63; H, 5.90; $OCH_3$, 15.58). A maximum in the ultraviolet absorption spectrum occurs at 280 mμ (log ε 3.42). The product of methylation is, therefore, identical in all respects with 8-O(-β-D-glucopyranosyl)-β-peltatin (II),[3] previously isolated from *P. peltatum.*

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[1] J. L. Hartwell, J. M. Johnson, D. B. Fitzgerald and M. Belkin, THIS JOURNAL, **75**, 235 (1953).

[2] J. L. Hartwell, *ibid.*, **69**, 2918 (1947); J. L. Hartwell and W. E. Detty, *ibid.*, **70**, 2833 (1948); **72**, 246 (1950).

[3] A. Stoll, A. von Wartburg, E. Angliker and J. Renz, *ibid.*, **76**, 5004, 6413 (1954).

[4] J. L. Hartwell and W. E. Detty, *ibid.*, **72**, 246 (1950), reported the melting point of α-peltatin, which was not quite free of β-peltatin, as 230.5–232.5° and the optical rotation as $[\alpha]^{20}\mathrm{D}$ −120° in chloroform. The somewhat lower values seem to be due to the small admixture of β-peltatin; this was not the case with our preparations which were obtained from the uniform glucoside.

[5] Our thanks are due to Messrs. S. B. Penick Co., New York, for making available a sample of α peltatin.