ing at room temperature overnight, the reaction mixture was poured into water and extracted with benzene. The benzene solution was washed with water, dried and concentrated. Crystallization from acetone gave 251 mg. (83%) of 2,4b-dimethyl-2-acetyl-7-ethylenedioxy-1,2,3,4,4aα,4b,-5,6,7,8,10,10aβ-dodecahydrophenanthrene-1,4-dione (XV), melting at 195–202°. Mixture melting point and infrared spectra established identity with the material prepared by methylation of XI.

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[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF AGRICULTURE, AND THE DEPARTMENT OF CHEMISTRY COLLEGE OF LETTERS AND SCIENCE, UNIVERSITY OF WISCONSIN]

Separation and Tentative Identification of Two New Sterols from Oats[1]

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Two new sterols and β-sitosterol were isolated from oats by a chromatographic separation of the azoyl esters. The upper zone sterol was a Δ^7-stigmastadiene-3β-ol with the most probable location of the second double bond at the 11(12)-position. The middle zone sterol appeared to be $\Delta^{5,11?}$-stigmastadiene-3β-ol. Oat oil sterols contain 11–14% of the Δ^7 sterol, 32–35% of $\Delta^{5,11?}$-stigmastadiene-3β-ol, 53–56% of β-sitosterol, and 0.4% of a $\Delta^{5,7}$-sterol.

Δ^7-Cholestenol is a minor constituent of commercial cholesterol[3] and a major constituent of rat skin.[4] The present study shows that a Δ^7-sterol occurs in substantial amounts in oats along with a new Δ^5-sterol. Crude oat sterols resemble the sterols from skin in that they react rapidly with the modified Liebermann–Burchard reagent (Fig. 1) in contrast to pure cholesterol[5,6] or β-sitosterol,[6] which develop a maximum color only after prolonged contact with the reagent.

Experimental[7]

Preparation of Crude Sterols.—Six hundred pounds of ground whole oats were extracted with petroleum ether, and a dark, viscous, tubid oil was obtained in 3% yield. On the addition of 5 volumes of acetone, a voluminous precipitate formed, and the clear solution of the oil was decanted from the residue after settling. The clear oil was saponified with alcoholic KOH under N_2 and in the presence of pyrogallol, and the unsaponifiable matter, 2.5% of the oil, was taken up in a minimum amount of boiling petroleum ether, and stored at 0° for several days. The colorless precipitate representing 24.5% of the original non-saponifiable fraction was stirred in chloroform or carbon tetrachloride and the poorly soluble *n*-aliphatic alcohols filtered off. The solution yielded crude sterols, m.p. 130–133°. Purified *via* the digitonide,[4] the sterol mixture melted at 137.5°, and showed maxima in alcohol at 265, 271.5, 281 and 293 mμ. The intensities of these bands indicated the presence of 0.41% of a $\Delta^{5,7}$-sterol.

Chromatography.—Azoyl esters were prepared by refluxing 1.0 g. of dry crude sterol and 0.9 g. of *p*-phenylazobenzoyl chloride with 10 ml. of pyridine for two hours. The mixture was chilled, precipitated with cold water, filtered and thoroughly washed with water. The dry mixed esters were taken up in 20 ml. of warm benzene, filtered to remove most of the pyridinium salt, and 180 ml. of petroleum ether (Skellysolve C) added to the filtered solution. The best esterification achieved was 65%.

A Zechmeister column, 7.6 cm. inside diameter, was treated with silicone oil[4,8] and prepared by packing a slurry of two parts of silicic acid[9] and one part of Celite 503 in petroleum ether under pressure. Without pressure the flow rate through the column was 5–6 ml. per minute. The esters were adsorbed on the first cm. of the column and a 3:1 Skelly C–benzene mixture was then passed through the column until the esters moved about 2 cm. The developer was gradually changed to 5.5:1 Skelly C–benzene and the column was run for 44 hours without further attention. The descending order of the bands and the amounts of ester recovered in a typical run were: 1 cm., pyridinium salt; 23 cm., space; 2 cm., "upper zone" ester (62 mg.); 1.5 cm., space; 4 cm., "middle zone" ester (132 mg.); 4 cm., space; 6 cm., "lower zone" ester (224 mg.); 7 cm., space; filtrate, *n*-aliphatic ester (114 mg.). Unesterified sterol from the top of the column brought the total recovery to 95%.

Properties of the Azoyl Esters.—The upper zone ester melted at 209° after two crystallizations from benzene–ethyl alcohol. These crystallizations resulted in a negligible loss of material and the melting point was unchanged on further recrystallizations from benzene.

Anal. Calcd. for $C_{42}H_{56}O_2N_2$: C, 81.30; H, 9.03. Found: C, 81.02; H, 9.12.

The middle zone ester was rechromatographed and the extremities of the zone discarded. After two crystallizations from benzene–ethyl alcohol the ester melted at 191°. The lower zone ester melted at 181°. Neither melting point was changed by further crystallization.

In the hydrolysis of these esters 4% KOH[4] caused considerable discoloration of the upper and middle zone sterols although the lower zone ester hydrolyzed satisfactorily. An empirical mixture which gave complete hydrolysis of many azoyl esters without discoloration was 3 ml. of 8% KOH in 70% ethanol, 7 ml. of ethanol, 2 ml. of water and 5 ml. of benzene for each 150 mg. of azoyl ester. Hydrolysis was continued on the steam-bath until solution was complete, one hour usually being sufficient. More benzene was added for very insoluble esters.

Upper Zone Sterol.—Hydrolysis of the azoyl ester yielded long needles on crystallization from methanol, m.p. 145°. The sterol contained 2.7% of a $\Delta^{5,7}$-sterol as measured by the ultraviolet spectrum. The sterol gave a Liebermann–Burchard reaction similar to that of the Δ^7-sterols[5,6] (Fig. 1), $[\alpha]^{28}D$ +8.75 ± 2° (30 mg. in 2.5 ml., corrected for 7-dehydrostigmasterol). The sterol could be precipitated by digitonin.

Anal. Calcd. for $C_{29}H_{48}O$: C, 84.40; H, 11.73. Found: C, 84.37; H, 11.85.

Derivatives.—The acetate of the upper zone sterol crystallized from ethanol in plates, m.p. 155°, $[\alpha]^{29}D$ +7.0 ± 2° (24 mg. in 2.5 ml., corrected for 7-dehydrostigmasterol).

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(2) Shell Oil Company Fellow, 1951–1952.

(3) L. F. Fieser, THIS JOURNAL, **73**, 5007 (1951).

(4) D. R. Idler and C. A. Baumann, *J. Biol. Chem.*, **195**, 623 (1952).

(5) P. R. Moore and C. A. Baumann, *ibid.*, **195**, 615 (1952).

(6) (a) D. R. Idler and C. A. Baumann, *ibid.*, in press; (b) summary given at the A.C.S. Meeting, Milwaukee, Wis., April, 1952.

(7) Melting points are corrected. All solutions for rotations were prepared in 2.5 ml. of chloroform solution, and the measurements made with a Schmidt and Haensch polarimeter No. 52-b with monochromator. Ultraviolet absorption spectra were taken of ethanol solutions. We are indebted to C. H. Schroeder of the Department of Biochemistry for the carbon and hydrogen analyses.

(8) General Electric Company "dri film" 9987.

(9) Analytical grade specially prepared for chromatography by the method of Ramsay and Patterson. Mallinckrodt Chemical Works.

Anal. Calcd. for $C_{31}H_{50}O_2$: C, 81.88; H, 11.08. Found: C, 81.80; H, 11.25.

The benzoate crystallized from acetone in plates, m.p. 177°, $[\alpha]^{29}D$ +13.4 ± 2° (19.6 mg. in 2.5 ml., corrected for 7-dehydrostigmasterol).

Reduction of the Upper Zone Acetate.—There was no uptake of hydrogen when the acetate was shaken for 30 minutes with Adams catalyst in ethyl acetate. However, in glacial acetic acid the reduction of 25.8 mg. of the acetate was 98% complete for one double bond on shaking for 6 minutes with 16 mg. of Adams catalyst, and the theoretical amount, 1.3 ml., was taken up within 20 minutes. Shaking was continued for three hours to complete the migration of the double bond to the 8(14)-position.[10] The reduction product crystallized from ethanol in plates, m.p. 114°, yield 22 mg. Pure $\Delta^{8(14)}$-stigmastenyl acetate did not depress the melting point. Alkaline hydrolysis of the two acetate preparations yielded plates out of methanol, m.p. 115°, mixed m.p. 115°. Both gave identical Liebermann–Burchard reactions (Fig. 1). The infrared spectra of the two preparations were identical and greatly resembled that of $\Delta^{8(14)}$-cholestenol.[11]

Titration with Perbenzoic Acid.—On standing for five days at −5° in an excess of perbenzoic acid in $CHCl_3$, 13 mg. of the upper zone acetate took up 1.42 mg. of oxygen, equivalent to 3.1 atoms of oxygen per mole of sterol. Under the same conditions 13 mg. of Δ^7-cholestenyl acetate took up 0.96 mg. of oxygen, equivalent to 1.97 atoms of oxygen per mole of sterol.

Middle Zone Sterol.—Hydrolysis of the azoyl ester, and crystallization from methanol gave platelets which melted at 137°, $[\alpha]^{26}D$ −37.6 ± 3° (23.7 mg. in 2.5 ml.). The sterol could be precipitated by digitonin. No maxima were found in the ultraviolet region of the spectrum. The sterol gave a Liebermann–Burchard reaction similar to that of β-sitosterol (Fig. 1).

Anal. Calcd. for $C_{29}H_{48}O$: C, 84.40; H, 11.73. Found: C, 84.35; H, 11.87.

Derivatives.—The acetate crystallized in plates from ethanol, m.p. 134°, $[\alpha]^{26}D$ −39.7 ± 2° (47.3 mg. in 2.5 ml.).

Anal. Calcd. for $C_{31}H_{50}O_2$: C, 81.88; H, 11.08. Found: C, 81.83; H, 11.21.

The benzoate crystallized out of acetone in plates, m.p. 157°, $[\alpha]^{26}D$ −11.8 ± 2° (32 mg. in 2.5 ml.).

Anal. Calcd. for $C_{36}H_{52}O_2$: C, 83.68; H, 10.15. Found: C, 83.56; H, 10.25.

Reduction of the Middle Zone Acetate.—The acetate did not absorb hydrogen when shaken for 30 minutes with Adams catalyst in ethyl acetate. In glacial acetic acid, however, the reduction of 30.8 mg. of the acetate was 96% complete for two double bonds after 8 minutes of shaking with 18 mg. of catalyst, and the theoretical amount of 3.04 ml. was taken up within 20 minutes. The reduced acetate crystallized from ethanol in plates, m.p. 134°, and the mixed melting point with authentic stigmastanyl acetate, m.p. 136°, was 135.5°, yield 28 mg. The starting material depressed the melting point. The optical rotation of the reduction product, $[\alpha]^{28}D$ +15.5 ± 2° (20 mg. in 2.5 ml.), also agreed with that of stigmastanyl acetate. Alkaline hydrolysis gave plates from methanol, m.p. 135.5°, undepressed by stigmastanol. The infrared spectra of the reduced middle zone sterol and of its acetate were identical with those of stigmastanol and its acetate, respectively.

Titration with Perbenzoic Acid.—On standing at −5° for three days in the presence of an excess of perbenzoic acid in chloroform, 15.2 mg. of the middle zone sterol took up 1.18 mg. of oxygen. This is the theoretical amount for two atoms of oxygen per mole of sterol. Similar results were obtained with the acetate.

Lower Zone Sterol.—Regeneration of the lower zone azoyl ester yielded needles, m.p. 140°, $[\alpha]^{27}D$ −37.1 ± 2° (42.4 mg. in 2.5 ml.). The sterol gave a Liebermann–Burchard reaction similar to that of β-sitosterol (Fig. 1), and there was no depression on mixed melting point with β-sitosterol. The acetate crystallized from ethanol in plates, m.p. 129.5°, undepressed by β-sitosteryl acetate, $[\alpha]^{27}D$ −42 ± 3° (31.9 mg. in 2.5 ml.). The benzoate crystallized from acetone in plates, m.p. 147°, undepressed by β-sitosteryl benzoate.

(10) H. Wieland and W. Benend, *Ann.*, **554**, 1 (1943).

(11) D. R. Johnson, D. R. Idler, V. W. Meloche and C. A. Baumann, THIS JOURNAL, **75**, 52 (1953).

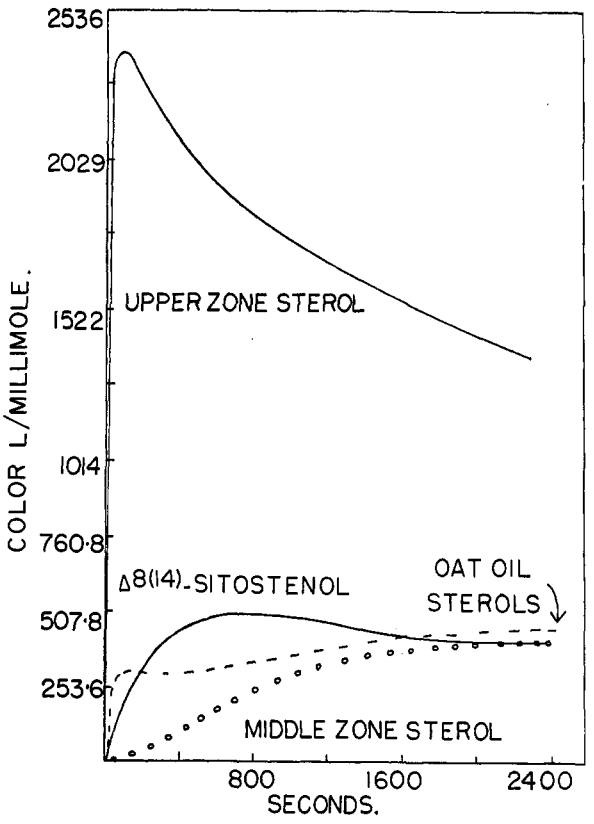

Fig. 1.—Reactivity of the sterols from oats with the modified Liebermann–Burchard reaction.

Infrared Spectra.—The spectra were recorded with a Baird Associates Model B recording infrared spectrophotometer with a sodium chloride prism. The crystalline sterols were prepared as solid films about 0.05 mg./mm.^{2} thick by fusion between rock salt plates under nitrogen and quickly cooling to room temperature. Spectra were taken not only of the three sterols from oats, but also of certain appropriate related sterols. Cholesterol, β-sitosterol, γ-sitosterol and stigmasterol, all of which have isolated 5-unsaturation, were shown to possess a characteristic band pattern having significant absorption centers at or near 9.42 μ (1061 cm.$^{-1}$), 9.77 μ (1023 cm.$^{-1}$), 10.46 μ (956 cm.$^{-1}$), 11.34 μ (882 cm.$^{-1}$), 11.90 μ (840 cm.$^{-1}$), 12.48 μ (801 cm.$^{-1}$) and 13.45 μ (743 cm.$^{-1}$). Δ^7-Cholestenol, Δ^7-ergostenol and α-spinasterol showed a common pattern of bands characteristic of the isolated 7-unsaturated sterol nucleus at 9.08 μ (1101 cm.$^{-1}$), 9.5 μ (1053 cm.$^{-1}$), 9.80 μ (1020 cm.$^{-1}$), 10.25 μ (976 cm.$^{-1}$) and 10.36 μ (966 cm.$^{-1}$) (except when interfered with by the 10.3 μ (970 cm.$^{-1}$) band of 22(23) unsaturation), 10.68 μ (937 cm.$^{-1}$), 11.81 μ (847 cm.$^{-1}$), 12.04 μ (830 cm.$^{-1}$), 12.55 μ (797 cm.$^{-1}$) and 13.75 μ (727 cm.$^{-1}$). $\Delta^{8(14)}$-Cholesterol, $\Delta^{8(14)}$-sitosterol and $\Delta^{8(14)}$-ergosterol showed a common pattern of bands characteristic of the $\Delta^{8(14)}$-sterol nucleus at 9.15 μ (1092 cm.$^{-1}$), 9.55 μ (1048 cm.$^{-1}$), 10.34 μ (967 cm.$^{-1}$), 10.64 μ (939 cm.$^{-1}$), 11.24 μ (890 cm.$^{-1}$), 11.58 μ (864 cm.$^{-1}$) and 11.80 μ (848 cm.$^{-1}$). Variation in the C_{24} substitution was found to introduce only slight spectral changes in this region, but none adequate for the identification of a methyl or ethyl group at C_{24}.

The spectrum of the oat sterol isolated from the lower zone of the chromatogram was identical to that of β-sitosterol. The spectrum of the middle zone sterol (Fig. 2) showed the band pattern of a Δ^5-sterol and was quite similar to that of β-sitosterol but it contained an additional strong band at 12.3 μ (8.13 cm.$^{-1}$) and a weak one at 6.15 μ (1625 cm.$^{-1}$). Furthermore the weak bands at 11.34 μ (880 cm.$^{-1}$) and 12.48 μ (801 cm.$^{-1}$) in the spectrum of β-sitosterol were shifted to 11.30 μ (885 cm.$^{-1}$) and 12.40 μ (806 cm.$^{-1}$), respectively, in the spectrum of the middle zone sterol from oats. There were also minor differences between the intensities of certain common bands.

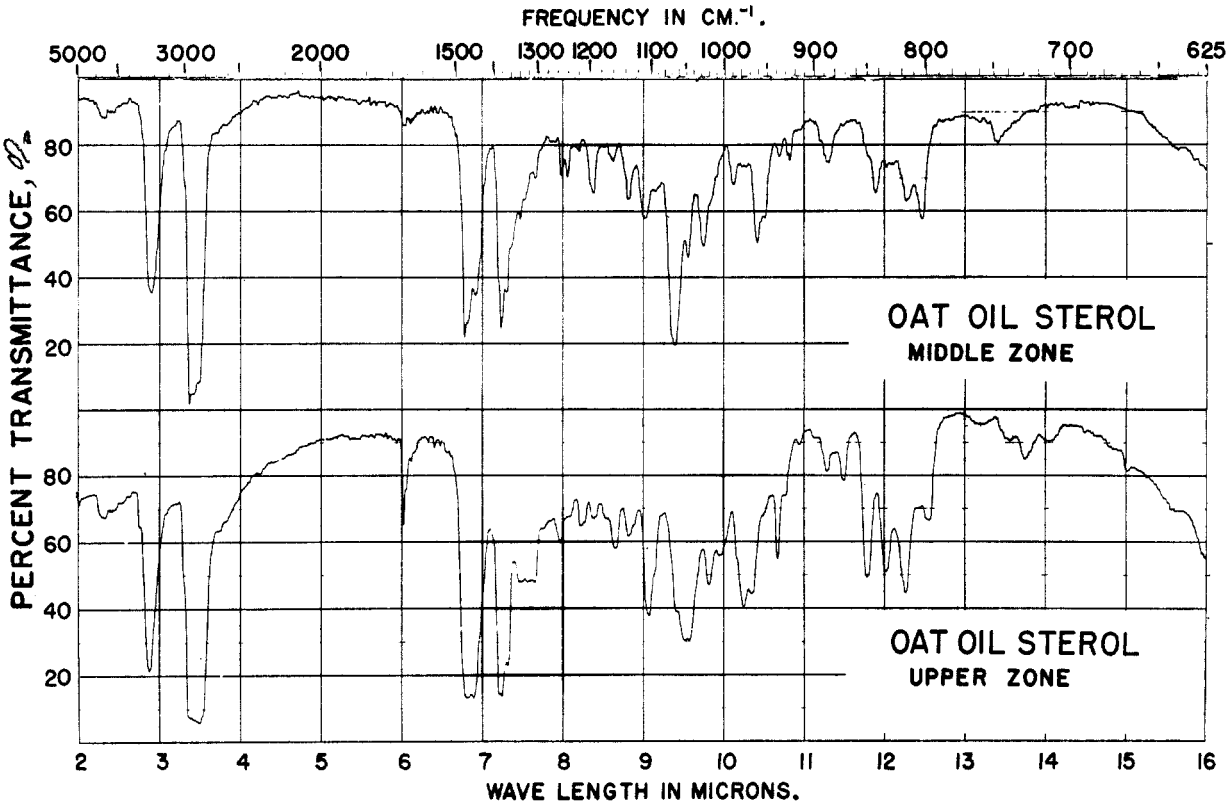

Fig. 2.—Infrared spectra of oat oil sterols: NaCl prism, 25°, effective thickness of sample *ca.* 0.05 mg./mm.².

The spectrum of the upper zone sterol (Fig. 2) closely resembled those of sterols containing an unconjugated double bond in the 7-position: Δ^7-cholestenol,[11] Δ^7-ergostenol and α-spinasterol. In addition bands were present at 12.28 μ (782 cm.$^{-1}$), 11.30 μ (885 cm.$^{-1}$) and in the region 7.5–7.7 μ (1330–1300 cm.$^{-1}$), and small shifts were noted in certain weak bands. The spectrum did not show the strong band at 10.3 μ (970 cm.$^{-1}$) characteristic of the *trans*-22(23)-double bond, nor the features at 3 μ, 6 μ and in the fingerprint region that have been associated with a conjugated system.

Discussion

Structure of the Middle Zone Sterol $\Delta^{5,11(?)}$-Stigmastadiene-3β-ol.—The middle zone sterol resembled β-sitosterol in the rate and intensity of the Liebermann–Burchard reaction, and in yielding stigmastanol on reduction. Rotational differences between the new sterol and its acetate and benzoate coincided with established differences for Δ^5-stenols (Table I), and its infrared spectrum also showed most of the characteristics of a Δ^5-stenol. The middle zone sterol differed from β-sitosterol in that it absorbed two mols of hydrogen and two atoms of perbenzoate oxygen.

Several properties argue against the location of the second double bond in the side chain. Double bonds in the side chain do not alter the chromatography of known steryl azoates,[12] but the middle zone sterol was separated from β-sitosterol by chromatography. The second double bond resisted hydrogenation in neutral medium under conditions adequate for the reduction of the 22(23)- or the 24(25)-bonds.[13] Furthermore, the infrared spectrum of the sterol lacked the strong band characteristic of the 22(23)-bond,[14] while the melting points and rotations of derivatives differed significantly from those of fucosterol ($\Delta^{5,24(28)}$-stigmastadienol).[15]

Most of the possible nuclear positions could also be eliminated. The spectra in the infrared and the ultraviolet both indicated the absence of a conjugated system, eliminating positions 3(4) and 7(8). The other possible positions in ring A are ruled out by the absence of vicinal effects[16] on optical rotation and by the failure of the sterol to dehydrate[17] to a sitostadiene in weak alcoholic HCl. Acid hydrogenation of the sterol yielded stigmastanol rather than the 8(14)-stenol that would result from the hydrogenation of positions 7(8), 8(9) or 8(14).[10] These positions are also ruled out by the failure of the sterol to give a rapid Liebermann–Burchard reaction. This failure also makes the 9(11)-position unlikely, since the latter would be expected to migrate to a position giving a positive Tortelli–Jaffe reaction[18] or a rapid Liebermann–Burchard reaction.[6] The ease and continuity of hydrogenation also suggests the absence of a 9(11)-double bond. The infrared spectrum of the sterol lacks the features characteristic of 14(15) stenols,[11,19] and the second double bond consumes only one atom of O in the perbenzoate titration instead of the two taken

(12) K. Ladenburg, E. Fernholz and F. S. Wallis, *J. Org. Chem.*, **3**, 294 (1938).

(13) H. Wieland, F. Rath and W. Benend, *Ann.*, **548**, 19 (1941).

(14) R. N. Jones, THIS JOURNAL, **72**, 5322 (1950).

(15) H. B. MacPhillamy, *ibid.*, **64**, 1732 (1942).

(16) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1949, pp. 204–219.

(17) O. Rosenheim, *Biochem. J.*, **23**, 47 (1928).

(18) Reference 16, p. 245.

(19) D. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch and C. V. Wood, *J. Chem. Soc.*, 2402 (1951).

TABLE I

DIFFERENCES IN MOLECULAR ROTATION BETWEEN DERIVATIVES OF OAT STEROLS AND OF Δ^5- AND Δ^7-STENOLS

	Molecular rotation (M_D) of			M_D (deriv.) − M_D (sterol)	
	Sterol	Acetate	Benzoate	Acet.	Benz.
Upper zone sterol	+35 ± 8	+31 ± 8	+68 ± 8	−4	+33
Δ^7-Stenols[a]				−15 ± 15	+20 ± 14
Middle zone sterol	−155 ± 12	−180 ± 8	−61 ± 8	−25	+94
Δ^5-Stenols[a]				−35 ± 16	+81 ± 16
Lower zone sterol	−153 ± 8	−190 ± 12	.....	−37	.....

[a] Reference 16, p. 208.

up by a double bond at 14(15).[20] The other positions of ring D are regarded as unlikely because of the relatively weak shoulder at 3.28 μ (3050 cm.$^{-1}$) instead of the marked absorption at this wave length that has been attributed to steric strain in 5-membered rings containing a double bond.[19] Thus, there are objections to all possible positions except 11(12); tentative evidence in favor of this position is the presence of a weak band at 6.15 μ (1626 cm.$^{-1}$) in the spectrum of the sterol. This weak band has been attributed to C=C stretching in the 11(12)-position of the steroids.[21]

Structure of the Upper Zone Sterol $\Delta^{7,11?}$-Stigmastadiene-3β-ol.—The presence of a double bond at position 7(8) was indicated by the rate of reaction with the modified Liebermann–Burchard reagent (Fig. 1), by the molecular rotation of its derivatives (Table I), by its infrared spectrum (Fig. 2) and by the higher melting point of its acetate.[22] The uptake of one mole of hydrogen with the formation of $\Delta^{8(14)}$-stigmastenol indicated the presence of an additional double bond. This was confirmed by the uptake of three moles of oxygen by the sterol on contact with perbenzoic acid while Δ^7-cholestenyl acetate consumed two moles in a parallel experiment. A double bond at position 7(8) in the cholestenes has also been reported to consume two atoms of perbenzoate oxygen[20] and α-spinasterol to consume three.[23]

The physical constants of the upper zone sterol are quite similar to those of α_3-sitosterol[13,24] from wheat, and of γ-spinastenol (Table II). But α_3-sitosterol has been reported to consume only two atoms of perbenzoate oxygen, and γ-spinastenol, a reduction product of α-spinasterol, contains only one double bond, while the sterol from oats contains two double bonds and it consumes three atoms of perbenzoate oxygen. However, all three compounds appear to be Δ^7-sterols.

TABLE II

SIMILARITIES BETWEEN α_3-SITOSTEROL, γ-SPINASTENOL AND THE UPPER ZONE STEROL FROM OATS

	α_3-Sitosterol[a]		Upper zone sterol		γ-Spinastenol[b]	
	M.p., °C.	α_D	M.p., °C.	α_D	M.p., °C.	α_D
Free sterol	142–143	+ 5.2	145	+ 8.7 ± 2	144–145	+11
Acetate	152–153	+ 6.1	155	+ 7.0 ± 2	156–157	+ 8
Benzoate	173–175	+12.0	177	+13.4 ± 2	180.5	+13
Azoate	.....	....	209	.....	.....	..

[a] S. Bernstein and E. S. Wallis, THIS JOURNAL, 61, 1903 (1939). [b] D. H. R. Barton, *J. Chem. Soc.*, 1356 (1948).

Rotational data on the upper zone sterol, infrared spectrum, and hydrogenation in neutral and acid solution make it unlikely that the second double bond is located in the side chain or in ring A, while the absence of conjugation eliminates positions 5, 9(11) and 14(15). The absorption at 3.28 μ is not that expected from a sterol with a double bond in ring D.[19] These considerations eliminate all nuclear positions except 11(12). The presence of bands at 12.3 μ (782 cm.$^{-1}$) and 11.30 μ (885 cm.$^{-1}$) in the spectra of both the upper and middle zone sterols from oats suggest a common structural feature, and certain aspects of the Liebermann-Burchard reaction are also in harmony with the presence of an 11(12)-double bond in both sterols. α-Spinasterol and ergosterol form less intense chromophores than Δ^7-cholestenol and 7-dehydrocholesterol, respectively,[6] whereas the upper zone sterol forms a more intense chromophore than Δ^7-cholestenol. This would be expected if the 11(12)-double bond moved into conjugation with the Δ^7-bond under the influence of the reagent. On the other hand the middle zone sterol was not fast acting, indicating that its second double bond did not contribute to the chromophore by forming a conjugated system; conjugation between a double bond at 11 and the remote 5-position would be less likely than between double bonds at 11 and 7.[25]

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(20) J. C. Eck and E. W. Hollingsworth, THIS JOURNAL, **63**, 2986 (1941).

(21) R. N. Jones, P. Humphries, E. Packard and K. Dobriner, *ibid.*, **72**, 86 (1950).

(22) D. H. R. Barton, *J. Chem. Soc.*, 1116 (1946). Examples of Δ^7-phytosterols that melt lower than their acetates include α-spinasterol, γ-spinastenol, 7-dehydrositosterol, 7-dehydrostigmasterol, ergosterol and Δ^7-ergostenol. Other sterols usually melt higher than their acetates.

(23) E. Fernholz and M. L. Moore, THIS JOURNAL, **61**, 2467 (1939).

(24) S. Bernstein and E. S. Wallis, *ibid.*, **61**, 1903 (1939).

(25) We propose the names "Δ^5-avenasterol," and "Δ^7-avenasterol," *Avena*, oats, for these sterols.